California Environmental Protection Agency

Air Resources Board

California Ambient Dioxin Air Monitoring Program
(CADAMP)

Quality Assurance Project Plan

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1.0 INTRODUCTION

The mission of the California Ambient Dioxin Air Monitoring Program (CADAMP) is to quantify the average ambient concentrations of airborne dioxins, furans, and dioxin-like polychlorinated biphenyls (PCBs) in two large urban regions of California over a two-year period. Under this program, the California Air Resources Board (ARB) will evaluate potential health impacts, assess the need for additional risk management strategies, and identify areas where additional study may be required. The ambient air monitoring program is one of three elements of an initiative proposed by the ARB.[1] The other two elements of the initiative address source level measurement of dioxin, furan, and dioxin-like PCB emissions from stationary sources and from motor vehicles. Only the ambient air monitoring program will be addressed in this document.

Ambient air monitoring for dioxins, furans and PCBs will be conducted over a two-year period in the San Francisco Bay Area and the South Coast Air Basin. The results of the monitoring will be summarized as monthly and quarterly averages to show any seasonal variations in ambient concentrations due to changing emissions and/or meteorological effects. The results will also be assessed as annual averages to characterize risk in the ambient air.

Within ARB, the Monitoring and Laboratory Division (MLD) will have lead responsibility for implementation of the ambient air monitoring program and will submit results, for use in risk characterization and risk management, to the Stationary Source Division (SSD).

1.1 BACKGROUND/PROBLEM

There is growing concern about overall exposure to dioxins in California, which includes exposure due to airborne emissions. Dioxins and furans are highly toxic chemicals that are formed as unwanted by-products during the combustion of materials and the manufacture of certain chlorinated chemicals. The ARB and United States Environmental Protection Agency (U.S. EPA) have identified dioxins as toxic air contaminants (TAC) and hazardous air pollutants (HAP), respectively. Various studies, including the U.S. EPA's "Draft Dioxin Reassessment," have shown that dioxins can cause cancer and other health problems including birth and developmental defects, and liver damage.[2] Dioxins have also been shown to affect hormone levels and alter cellular function. In addition, the California Office of Environmental Health Hazard Assessment (OEHHA) report, “Prioritization of Toxic Air Contaminants Under the Children’s Environmental Health Protection Act,” lists dioxins as one of five toxic air contaminants that may cause children and infants to be especially susceptible to illness.[3]

Dioxins and furans are emitted into the atmosphere from a variety of sources including cars and trucks, waste incineration, chemical manufacturing plants, and other industrial sources that burn fuel. These toxic chemicals can be inhaled directly or can contaminate vegetation and be eaten by animals and humans. Dioxins then accumulate in the body. Fugitive dust and reservoir sources, such as soil, sediment, and manufactured materials

which contain dioxins that are temporarily stored, but may later be released into the circulating environment, may also be a significant source of dioxins.

Dioxin has become a significant issue in the San Francisco Bay area due to concerns over elevated levels of dioxins in the waters of the San Francisco Bay. In 1994, OEHHA issued a public health advisory based on the presence of pollutants, including dioxins, in San Francisco Bay fish. As a result, the Bay has been listed under Section 303(d) of the Federal Water Pollution Control Act as a water body that fails to meet water quality standards for dioxins. [4]

The U.S. EPA has been conducting ambient air dioxin monitoring as part of the National Dioxin Air Monitoring Network (NDAMN).[5] However, the target monitoring areas for NDAMN, selected to determine background atmospheric levels of dioxins, furans, and dioxin-like PCBs, are generally in rural areas around the country. Specifically, NDAMN sites are located in agricultural areas where livestock, poultry, and animal feed crops are grown. NDAMN sites are expected to provide data to evaluate long-range transport and deposition air models. Currently there are two California NDAMN sites; Fort Cronkhite in the San Francisco Bay Area and Rancho Seco in the Central Valley. The Fort Cronkhite site, which began operation in November 2000, was set up by the Bay Area Air Quality Management District (BAAQMD) using resources provided by the U.S. EPA. The Rancho Seco site began operation in May 2001.

Ambient air quality data for dioxins, furans, and dioxin-like PCBs in California are very limited, particularly for populated areas. One ambient sampling study took place in the South Coast air basin, however those results were generated using higher levels of detection than are being sought in this study, and are now more than ten years old. [6]

Public and environmental groups have questioned the environmental fate and the potential for public health impacts from these chemicals. To date, there has been only limited information collected on dioxin source emissions and ambient air concentrations in California, which has made it difficult to adequately address these health concerns. Long-term data for ambient airborne levels of dioxins and furans in California is necessary to assess changes in potential health impacts and to provide baseline information for use as the Board considers potential risk reduction strategies.

1.2 SPECIFIC PROJECT OBJECTIVES

- To determine and assess airborne concentrations of dioxins, furans, and dioxin-like PCBs on regional and sub-regional scales in populated air basins in the state expected to be impacted by stationary and mobile emissions sources.

- To provide information to the SSD for use in considering the need for further emission reduction strategies and identification of areas where additional study may be needed.

- To provide additional information, whenever possible, for the Children's Environmental Health Protection monitoring program (Senate Bill 25) by using the same sampling sites. [7]

- To report monthly, quarterly and yearly average ambient air concentrations for use by the SSD in risk characterization and risk management.

- To provide a statement of data usability to the SSD along with the monitoring results by following a strict QA/QC program and using appropriate data quality indicators.

- To the extent feasible, coordinate the monitoring procedures with the U.S. EPA NDAMN program to allow comparison of CADAMP and NDAMN monitoring results.

1.3 SUMMARY OF MONITORING PROGRAM

Samples will be collected at five urban sites in the San Francisco Bay Area and four urban sites in the South Coast Air Basin. A contract laboratory specializing in the analyses of dioxins/furans and PCBs will analyze the samples.

U.S. EPA Method TO-9A will be used as the basis for the ambient air sampling and analytical procedures for the CADAMP. [8] A sampler manufactured by Thermo- Andersen and referred to as the Polyurethane Foam Sampler (PUF) - Special will be used as the primary CADAMP sampler. [9] The sampler collects atmospheric particulate material on a quartz fiber filter (QFF) which forms the initial portion of the sampling train. Vapor-phase constituents pass through the QFF and impinge on pre-cleaned polyurethane foam plugs (PUFs) and XAD-2 resin inside a glass cartridge.

The samplers will be operated in the standard configuration described in Method TO-9A, but the sampling period will be extended from 24 hours to 576 hours (24 out of every 28 days). The PUF will be augmented with XAD-2 resin between two portions of the PUF, forming a PUF-XAD-PUF sandwich. QFFs and PUF/XAD media will be combined and extracted per U.S. EPA Method TO-9A, and analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). A detection limit of approximately one femtogram per cubic meter (1 fg/m^3) for 2,3,7,8-TCDD should be achieved by using the extended sampling period. Validation studies have been conducted by the State of Connecticut Department of Environmental Protection to evaluate the use of extended sampling periods for the measurement of PCDDs and PCDFs in ambient air. [10]

In order for the information derived from this study to be reliable, the quantitative sampling and analysis procedures used to monitor at these extremely low levels must be followed carefully, and approved quality assurance/quality control (QA/QC) procedures must be stringently applied throughout the study.

2.0 PROJECT MANAGEMENT

The ARB is responsible for managing and overseeing the CADAMP. Within ARB, the CADAMP will involve the Stationary Source Division (SSD), the Monitoring and Laboratory Division (MLD) and the Office of Information Services (OIS). SSD prepared the Budget Change Proposal (BCP) that provided the program direction and the funds necessary to implement and operate the ambient air monitoring network. [1] SSD is the client for the ambient data produced by the MLD monitoring program. Within SSD, the Emissions Evaluation Section of the Emissions Assessment Branch will be the program lead.

Within MLD, the Quality Management Branch (QMB) and the Air Quality Surveillance Branch (AQSB) will have specific responsibilities. The QMB's Operations Planning and Assessment Section (OPAS) will act as the lead section for the MLD monitoring program. OPAS will act as the program coordinator for the ambient monitoring program, including coordination activities within MLD, and with other Divisions, local air districts and the U.S. EPA. OPAS will also serve as the contract manager for the analytical contract laboratory. AQSB will coordinate sampler specific issues and will conduct the sample collection at two sites. The QMB's Quality Assurance Section (QAS) will coordinate quality assurance activities including field audits, performance checks and parallel sampling operations (i.e., with NDAMN), and will implement a laboratory audit program.

OIS will be responsible for designing and programming for the database that will be used to archive electronic data and generate reports for the CADAMP.

The external agencies that provide resources for CADAMP field operations are the Bay Area Air Quality Management District (BAAQMD) and the South Coast Air Quality Management District (SCAQMD). The U.S. EPA will supplement the CADAMP database with data from their California NDAMN sampling sites. The U.S. EPA will also participate in an inter-laboratory comparison of performance evaluation samples. **Figure 1** shows the organization of the CADAMP.

2.1 ARB ROLES AND RESPONSIBLITIES

2.1.1 Stationary Source Division

Mr. Don Ames, Assistant Division Chief of the Stationary Source Division (SSD) will be responsible for policy oversight for the program. Mr. Richard Boyd, Manager of the Emissions Evaluation Section (EES) will have supervisory oversight for the program and will be the client for all data generated. Ms. Michelle Komlenic of EES will be SSD staff lead. The EES will:

- Review and approve MLD CADAMP documents (e.g., QAPP).
- Act as the overall database manager and generate and release reports, as appropriate.
- Coordinate communications with parties outside the ARB regarding CADAMP.

- Ensure results are provided to local air districts for a two-week review period prior to public release.
- Release monitoring results to the public, as appropriate.
- Review risk factors and describe means of comparing results.
- Perform analysis of ambient data and source emissions data to determine any correlation.
- Evaluate the need for control strategies, as appropriate.
- Act as the program lead for public outreach activities.
- Create and update the CADAMP fact sheet and primary dioxin web site.

2.1.2 Monitoring Laboratory Division

Mr. William V. Loscutoff, the Monitoring and Laboratory Division Chief, has overall executive authority within MLD. Mr. Jeffrey P. Cook, the Quality Management Branch Chief, will have responsibility for coordinating the CADAMP within MLD.

Mr. Kenneth R. Stroud, the Air Quality Surveillance Branch Chief, will have responsibility for sampler specific issues (e.g., purchase, testing, installation, calibration, operation, repairs, modifications, and coordination with manufacturer) and the sample collection at two sites.

Mr. Webster Tasat, Manager of OPAS, will have supervisory oversight of the OPAS group. Within OPAS, Mr. Kevin Mongar will serve as lead staff, or Program Coordination Leader (PCL), and will provide the technical liaison between MLD, SSD, the local air districts, and the contract laboratory. The PCL will have responsibility for all operations planning, tracking and assessment aspects of the program. The PCL will ensure that high technical quality is maintained, that tasks adhere to a pre-established schedule, and that work is performed within budget.

Tasks that MLD is responsible for are listed below.

<u>Operations Planning and Assessment Section will:</u>

- Act as the primary contact between MLD and SSD, AQMDs, U.S. EPA and other stakeholders for CADAMP monitoring issues such as site selection, scheduling, and program planning and design.
- Prepare and update the Quality Assurance Project Plan (QAPP) for the CADAMP.

- Prepare and update the Field Operation procedures for the CADAMP.

- Coordinate MLD's activities to ensure that reasonable timelines/deadlines are established for field work and report generation. Schedule meetings as necessary with SSD, AQSB and OIS to discuss project needs and to establish and ensure that schedules are met.

- Manage the laboratory contract. OPAS staff are responsible for writing the Request for Proposals (RFP), reviewing proposal bids, and awarding the contract within the scope of the RFP process.

- Coordinate with the contract laboratory to track progress and to ensure the contractor has met all aspects of the program requirements.

- Coordinate with the laboratory to ensure delivery of the correct type and number of sampling media to each of the sampling site shipping locations for the duration of the studies.

- Act as the overall field operations coordinator and contact between MLD and the AQMD and ARB sampling personnel for CADAMP field sampling activities (e.g., CADAMP specific sampling, procedural, scheduling, and laboratory issues with the exception of sampler SOP specific issues such as purchase, installation, operation, calibration or repairs).

- Provide training for ARB and air district technicians on Field Operation related issues (i.e., CADAMP specific procedures).

- Receive and review field data forms immediately following each sampling period to determine validity of samples based on field QC criteria. Contact sampling personnel to clarify any issues. Enter field data into the CADAMP database.

- Coordinate with the laboratory to insure delivery/receipt of all samples.

- Provide analysis instructions to the laboratory based on validation of field data and sample receipt conditions (i.e., instruct the laboratory on which samples to analyze).

- Coordinate with AQSB staff to resolve sampler issues.

- Receive and review the laboratory data reports. Perform laboratory data validation and coordinate revision/correction of data reports.

- Work with OIS and SSD to establish the CADAMP database.

- Enter the laboratory sample and quality control results into the CADAMP database.

- Evaluate and assess the monitoring results.
- Create and update the MLD portion of ARB's dioxin web pages.
- Track the progress of the project.

Quality Assurance Section will:

- Review appropriate CADAMP documents and approve appropriate quality assurance elements.
- Conduct sampler flow audits.
- Conduct contract laboratory system audits.
- Coordinate and implement the use of laboratory performance evaluation samples.
- Coordinate an inter-laboratory comparison study using the laboratory performance evaluation samples.
- Coordinate the collection of parallel field samples with the U.S. EPA NDAMN program.
- Submit laboratory system audit, flow audit, performance evaluation sample results, inter-laboratory comparison and parallel sampling reports to OPAS.
- Provide and update site reports on the MLD/QAS website.
- Conduct annual certification for the orifice transfer standards used to calibrate the samplers and conduct routine flow checks.

Air Quality Surveillance Branch (AQSB) will:

- Prepare a Standard Operating Procedure describing in detail all aspects of sampler operation including: sampler acceptance testing, sampler calibration and calibration criteria, sampler maintenance, and sampler operation.
- Purchase and provide equipment and sampling supplies specific to field sampling, including samplers, sampler parts, PUF glass sleeves, freezers, refrigerators, latex gloves, and recorder charts. Perform acceptance testing on purchased equipment.
- Develop sites as necessary for monitoring and ensure compliance with siting criteria. Install equipment. Make necessary arrangements for phone, power and security at the site.

- Provide training to air district technicians on the sampler SOP as needed.
- Coordinate sampler calibrations and repairs for all sites.
- Perform sample collection at the Boyle Heights and Wilmington sites.
- Coordinate with the manufacturer on and implement any modifications and improvements to the samplers.
- Conduct shop and field trials to validate sampler modifications.

2.1.3 Office of Information Services

Mr. William Welty, the Office of Information Services (OIS) Branch Chief, will have responsibility for coordinating the development of the CADAMP database within OIS. Mr. Gary Knops, Manager of the Mobile Source and Air Quality Systems Development Section, will have supervisory oversight of the development project.

The Office of Information Services will:

- Create a database to archive CADAMP data.
- Write computer programs to conduct electronic data validation, perform calculations, and generate reports based on queries.

2.2 AQMD ROLES AND RESPONSIBLITIES

2.2.1 Bay Area Air Quality Management District (BAAQMD)

The roles and responsibilities of the BAAQMD are described in a memorandum attached as APPENDIX A.

2.2.2 South Coast Air Quality Management District (SCAQMD)

The roles and responsibilities of the SCAQMD are described in a memorandum attached as APPENDIX B.

2.3 LABORATORY ROLES AND RESPONSIBLITIES

The analytical contract laboratory, AXYS Analytical Services, will have the following responsiblities, which are summarized from the contractual agreements.

- Provide QFF and PUF sampling media which has been cleaned and QC checked to meet the detection limit criteria listed in Table 6.

- Ship pre-spiked sampling media, with Chain-of-Custody (COC) document, to field locations as per the instructions provided by OPAS.

- Provide pre-paid Federal Express account billing and all packing materials and shipping containers for return shipment of samples.

- Notify OPAS PCL within 48 hours of receipt of all samples in a sample delivery group describing condition upon receipt and any COC discrepancies.

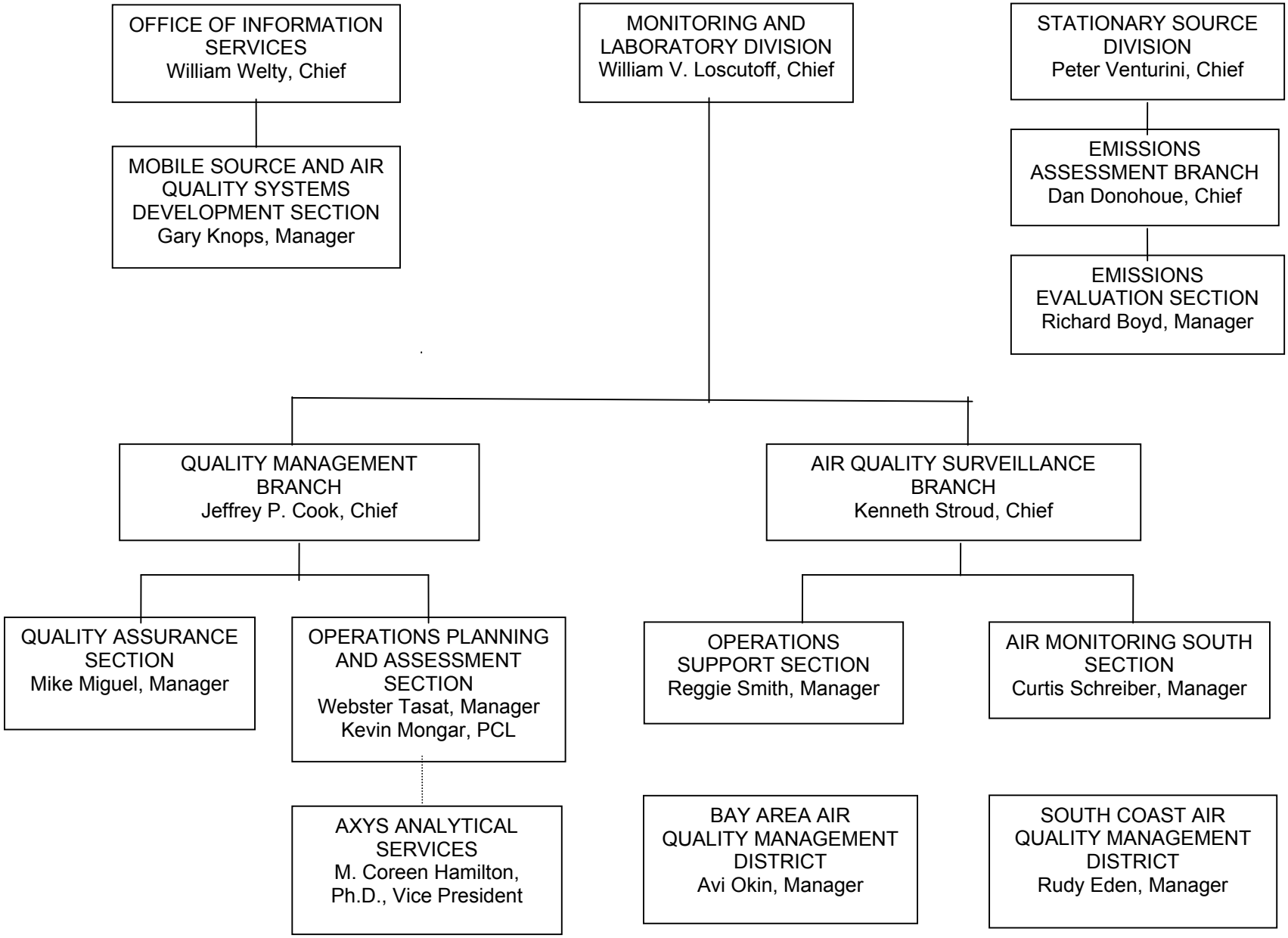
- Perform analysis of samples for PCDD, PCDF and PCBs as per the methods specified in this document.

- Submit analytical results report to the PCL within 30 days of receipt of the last sample in the sample delivery group, following the format described under Reporting Requirements and Deliverables in Section 7.16.

- Work with OPAS to amend and validate data as necessary. Respond to questions and make modifications to reports within 10 days of receipt of comments.

- Participate in an inter-laboratory comparison of performance evaluation samples.

Figure 1 CADAMP Organization Chart



3.0 MONITORING LOCATIONS

The purpose of this two-year program is to conduct ambient air dioxin, furan, and dioxin-like PCB monitoring in the San Francisco Bay Area and the South Coast air basin to better understand human exposure to these classes of compounds in urban areas. ARB staff originally proposed that four dioxin sampling sites be located in each of the two regions. However, monitoring at one additional site (Richmond), for a total of five CADAMP sites in the Bay Area, was requested by the SSD. Selection of individual sites was made in accordance with the objective of achieving population-oriented sampling.

The population-oriented nature of the state's program complements the rural sampling focus of the U.S. EPA's National Dioxin Air Monitoring Network (NDAMN). Together, the California program and U.S. EPA's NDAMN will help our understanding of exposure from multiple airborne pathways.

The sites selected for monitoring were located in populated areas a) with a record of elevated pollution levels, b) near potential sources of dioxin emissions, c) where other pollutant measurements of interest are made, and d) with the potential to relate dioxin concentrations in air transport pathways that lead to sensitive ecological areas such as agricultural lands, wetlands and marshes, and watersheds.

3.1 SAN FRANCISCO BAY AREA

The air monitoring network operated by the BAAQMD is extensive and provides a good base from which to consider dioxin sampling sites. The District's network of 25 stations produces a variety of criteria and air toxic pollutant measurements. In late 2001, two new, full monitoring stations (criteria and air toxics) were put into operation at schools in Oakland in Alameda County, and Crockett in Contra Costa County to support the state's Children's Environmental Health Protection Program. The District and the ARB operate these sites.

The five sites selected for dioxin monitoring in the Bay Area are described below with some of the factors that affected their selection. Detailed physical site descriptions can be found at the internet web addresses provided with each description below.

Oakland-Fruitvale (Lockwood Elementary School)

- Downwind of potential dioxin sources such as a heavily traveled freeway (I-880), an international airport, medium and heavy industry, and ship traffic.
- The community presently has no monitoring, reports high-density residential land use, and has documented elevated respiratory problems.
- The school is near dense commercial development and high surface vehicle traffic.
- The dioxin sampler was collocated with a Children's Environmental Health site that began operation in April 2001 (extensive criteria pollutant, toxic organic carbon gases, trace metals, diesel surrogate markers, PM10 and PM2.5, and PAH).

- At location with dense population of school children.
- Located near the Bay where deposited combustion materials could run-off to surface waters.
- www.arb.ca.gov/aqdas/siteinfo.php3?site=60998

Livermore (Old 1st Street)

- Located in an area with the highest number of days exceeding the state ozone air quality standard in the SF Bay Area Air Basin (1999).
- Livermore valley reported the second highest annual average concentration of PM10 in the SF Bay Area Air Basin (1999).
- Populated, fast growing area (Tri-Cities Area) downwind of emissions from the central Bay Area.
- Collocated with a site that includes air toxic measurements (VOC) made routinely as part of BAAQMD air toxic network. Notable high concentrations in the District for MTBE and methyl chloroform (1999) at this location.
- Hi-volume freeway upwind (I-680) and transecting the Livermore Valley (I-580).
- Source area for wood smoke from fireplaces.
- Agricultural operations in the Valley. Air transport corridor to agricultural and natural resources in the San Joaquin Valley.
- www.arb.ca.gov/aqdas/siteinfo.php3?site=60340

Crockett (John Swett High School)

- Located in the area of the highest 24 hour average and annual average SO_2 concentration in SF Bay Area Air Basin.
- Located near BAAQMD sites (Vallejo) with high toxic VOC concentrations (benzene).
- Collocated with Children's Environmental Health site established in the fall of 2001 at John Swett High School (extensive criteria pollutant, toxic organic carbon gases, trace metals, diesel surrogate markers, PM10 and PM2.5, and PAH).
- Close to several petroleum refineries with incidence of emissions impacting the area during upset conditions.
- Located downwind of several refineries (under the two dominant seasonal wind flow patterns in the area) and other medium to heavy industry in western and northern Contra Costa County.
- Representative of medium and small size towns typical of the northern tier of the County.
- Downwind of heavily traveled freeway (I-80) and shipping traffic transiting the San Francisco Bay and Delta.
- Primary air transport pathway to populated areas downwind and to tidelands, marshes, and Delta tributaries.
- *www.arb.ca.gov/aqdas/siteinfo.php3?site=07999*

San Jose (158 Jackson Street - *the original site was located at 120 N. 4th Street; the site was moved to Jackson Street in September 2002*)

- Location of highest concentrations of particulate matter (PM10), carbon monoxide (CO), and nitrogen dioxide (NO_2) in the SF Bay Area Air Basin,
- Site with highest elemental carbon and benzo(a)pyrene levels reported in the SF Bay Area Air Basin.
- Collocated with BAAQMD air toxic VOC sampling station, and extensive regular monitoring, wind patterns well characterized.
- Emission sources in the vicinity include fireplaces, multiple freeways, heavy surface vehicular traffic, and an international airport.
- Heavily populated area representative of southern Bay Area communities and air pathway to densely populated residential and agricultural areas to the south.
- www.arb.ca.gov/aqdas/siteinfo.php3?site=43382

Richmond (7th and Hensley)

- Located in vicinity of heavy industry and residential land uses.
- Monitoring exists for SO_2, H_2S, and air toxic gases.
- Sited in a community with interest in environmental justice.
- Several industrial source categories in community are suspected sources of dioxin.
- www.arb.ca.gov/aqdas/siteinfo.php3?site=07441

3.2 SOUTH COAST AIR BASIN

The four sites selected for dioxin monitoring in the South Coast air basin are described below with some of the factors that affected their selection.

Wilmington (Children's Center)

- Collocated with ARB Children's Environmental Health Protection Program (CEHP) monitors that include extensive criteria and air toxics measurements.
- In vicinity of satellite CEHP site at Hawaiian Elementary School.
- In area with heavy industry including multiple oil refineries with a combined refining capacity of over 250,000 barrels per day. Wilmington is also situated near the ports of Los Angeles and Long Beach, which are sources of diesel and fugitive emissions from bulk transport activities.
- There are an estimated 12 schools and childcare facilities in the area.
- Other sources of air pollution in Wilmington include neighborhood-scale sources such as dry cleaners, chrome plating operations, and service stations.
- Additional exposure data will be collected at the Wilmington Park Elementary School by researchers from the Southern California Particle Center and Supersite (SCPCS).
- www.arb.ca.gov/aqdas/siteinfo.php3?site=70996

Boyle Heights (Los Angeles Unified School District Science Center)

- Located at a prior ARB Children's Environmental Health Protection Program monitoring site.

- Proximity to heavily traveled surface streets used by heavy duty diesel trucks. Immediately downwind of freeways include 60, 5, 10 and 101.
- High number of children living in the community; Hollenbeck Middle School, has a student population of 2200. Theodore Roosevelt Senior High School, located directly across from Hollenbeck, is one of the largest high schools in Los Angeles County with an enrollment of over 5000.
- Approximately 16 schools and childcare centers (public and private) in the area encompassed by the 60, 5, 10 and 101 freeways.
- Collocated with activities of the Southern California Particle Center and Supersite that enables comprehensive assessment of aerometric data.
- www.arb.ca.gov/aqdas/siteinfo.php3?site=70993

Reseda (18330 Gault St.)

- Located at SCAQMD Reseda network air monitoring site that includes measurements of criteria pollutant gases, particulate matter, and meteorological parameters.
- Air quality and health effects research at this site by the Southern California Particle Center and Supersite (SCPCS).
- Reseda sampling site reported noticeable dioxin levels in a short-term air quality study performed in the mid-80s.
- Located in a part of the Basin with elevated relative levels of certain air toxics.
- Population center with a mix of light industry, commercial and residential uses nearby.
- Provides good spatial representation of population centers within the Basin.
- www.arb.ca.gov/aqdas/siteinfo.php3?site=70074

Rubidoux (5888 Mission Blvd.)

- Sampling coincides with Southern California Particle Center and Supersite (SCPCS) data collection program. The air monitoring site has also been used heavily for other aerometric research and much information will be available to supplement analyses of dioxin ambient data.
- South Coast AQMD has operated a fully instrumented site for several years at this location.
- Location of statewide high concentrations of PM and volatile constituents.
- Located sufficiently far downwind to be impacted by emissions from the greater South Coast Air Basin.
- www.arb.ca.gov/aqdas/siteinfo.php3?site=33144

Figure 2 San Francisco Bay Area Sampling Locations

Figure 3 Los Angeles Area CADAMP Sampling Locations

4.0 POLLUTANTS

The CADAMP samples will be analyzed for the 17 specific 2,3,7,8-substituted congeners of polychlorinated dibenzo-para-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), and their homologue totals, as well as 14 dioxin-like polychlorinated biphenyl (PCB) compounds, as listed in Table 1. Figure 4 shows the numerical substitution positions of the dioxin, furan, and PCB molecules.

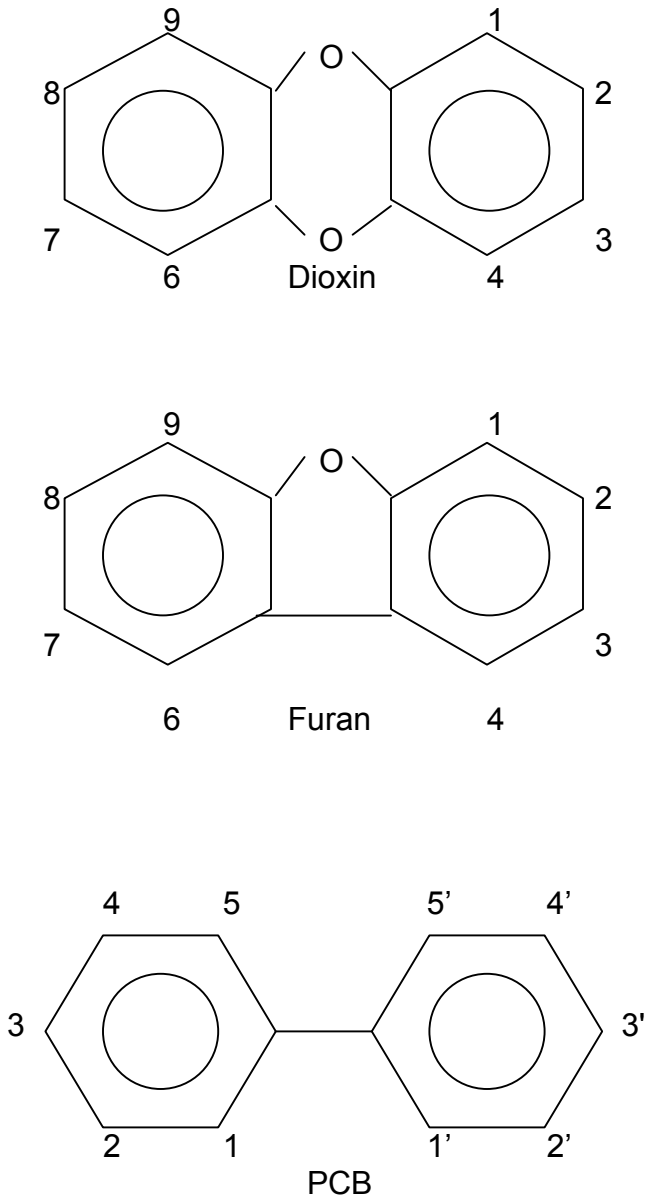


Figure 4 Dioxin, Furan, and PCB Substitution Pattern

Table 1 CADAMP Analytes

PCDDs	PCDFs
2,3,7,8-Tetra CDD (TCDD) 1,2,3,7,8-Penta CDD (PeCDD) 1,2,3,4,7,8-Hexa CDD (HxCDD) 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,6,7,8-Hepta CDD (HpCDD) 1,2,3,4,6,7,8,9-Octa CDD (OCDD)	2,3,7,8-Tetra CDF (TCDF) 1,2,3,7,8-Penta CDF (PeCDF) 2,3,4,7,8-PeCDF 1,2,3,4,7,8-Hexa CDF (HxCDF) 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-Hepta CDF (HpCDF) 1,2,3,4,7,8,9-HpCDF 1,2,3,4,6,7,8,9-Octa CDF (OCDF)
Total TCDD Total PeCDD Total HxCDD Total HpCDD Total PCDD	Total TCDF Total PeCDF Total HxCDF Total HpCDF Total PCDF
PCBs	
3,3’,4,4’-TeCB (PCB 77) 3,4,4’,5-TeCB (PCB 81) 2,3,3’,4,4’-PeCB (PCB 105) 2,3,4,4’,5-PeCB (PCB 114) 2,3’,4,4’,5-PeCB (PCB 118) 2’,3,4,4’,5-PeCB (PCB 123) 3,3’,4,4’,5-PeCB (PCB 126) 2,3,3’,4,4’,5-HxCB (PCB 156) 2,3,3’,4,4’,5’-HxCB (PCB 157) 2,3’,4,4’,5,5’-HxCB (PCB 167) 3,3’,4,4’,5,5’-HxCB (PCB 169) 2,2’,3,3’,4,4’,5-HpCB (PCB 170) 2,2’,3,4,4’,5,5’-HpCB (PCB 180) 2,3,3’,4,4’,5,5’-HpCB (PCB 189)	

5.0 MONITORING PROGRAM DESCRIPTION

The ARB, with support provided by the Bay Area and South Coast AQMDs, shall implement the CADAMP. U.S. EPA Method TO-9A will be used as the basis for the ambient air sampling and analytical procedures.

5.1 SITING CRITERIA

The detailed criteria for siting the samplers will follow state and federal procedures outlined in the California Air Resources Board's Standard Operating Procedures for Air Quality Monitoring and U.S. EPA regulations. [11,12] Each site has been given a specific site name and number. Sample inlets are between 2 to 15 meters above the ground surface. When samplers are collocated, the sample inlets must be at least 2 meters but less than 4 meters apart.

5.2 SAMPLING METHOD REQUIREMENTS

The CADAMP samplers will be operated in accordance with the "Field Operation of the California Ambient Dioxin Air Monitoring Program Sampling Network", www.arb.ca.gov/aaqm/qmosopas/dioxins/field_ops_v1.0.pdf , and the "Standard Operating Procedures for Air Quality Monitoring for Andersen Instruments Poly-Urethane Foam (PUF) Sampler Special" (SOP). [13] www.arb.ca.gov/aaqm/qmosopas/dioxins/equipment/puf_sop.pdf

The Field Operation document was prepared using the U.S. EPA's "Draft General Procedures for Operation of the National Dioxin Air Monitoring Network" and U.S. EPA Method TO-9A as guidance documents. [14] The sampler SOP includes procedures for the acceptance testing, installation, operation, calibration and quality control, and maintenance of the air samplers. The program will use modified high volume ambient air samplers adapted from Method TO-9A.

Method TO-9A specifies sampling for a 24-hour period for a total sample volume of 325 – 400 m^3. However, CADAMP will operate samplers 24 days out of a 28-day schedule (i.e., 24 days x 24-hours) for a target total sample volume of approximately 8300 m^3. The adaptation of Method TO-9A to a long duration sampling protocol has been validated by ENSR Corporation (B. Maisel and G. Hunt) for the State of Connecticut Department of Environmental Protection from 1993 – 1997 and is currently in use by the U.S. EPA NDAMN program. [9]

The sampling head (Figure 5.0.2 of the Field Operation document) includes two types of sampling media: a quartz fiber filter (QFF) and a glass cartridge containing two polyurethane foam plugs (PUF) with 10 grams of XAD-2 resin in between. The QFF will collect and retain particulate matter $\geq$ 0.6 microns, and the PUF/XAD/PUF will collect and retain gaseous phase compounds. The samplers will be operated for 13 periods annually. In order to achieve a target detection limit of 0.6 to 1.2 fg/m^3 for TCDD, which

is necessary to avoid non-detects in air, each sampling period consists of 24 days of sampling over a 28-day period. The weekly schedule will consist of 6 days of continuous operation followed by one day of inactivity. Each week, on the inactive day, the exposed QFF is retrieved and replaced, yielding four QFF composite samples per sampling period. The PUF/XAD/PUF cartridge is retrieved once at the end of the four-week sampling period. A complete sample is comprised of one PUF/XAD/PUF cartridge and four QFFs.

The laboratory responsible for sample analysis will provide pre-cleaned and certified QFFs and cartridges prepared in accordance with the procedures specified in Section 10 of Method TO-9A, modified as necessary to meet the detection limits listed in Table 6. All cartridges (to be used in active samplers and field blanks) will be pre-spiked by the laboratory with the isotopically labeled PCDD, PCDF and PCB compounds listed in Table 7. The laboratory will be provided with all relevant information regarding the monitoring schedule and site addresses, contacts, etc., and will be directly responsible for shipment of sampling media to field locations on-schedule. The laboratory will send the prepared, un-exposed samples to the District or ARB site operators.

On-site operators will conduct the sample collection and return the exposed samples to the laboratory. The chain of custody (COC) sheets will be completed by the on-site operators and transferred to the laboratory along with the samples. The CARB 28 Day PUF Field Sample Report Form (see Field Operation document) will be completed by the on-site operators and transferred to OPAS PCL at the same time that samples are shipped.

The laboratory will notify the ARB PCL within 48 hours of receipt of all samples in a sample delivery group (SDG). A SDG will consist of all samples from a given monitoring period (i.e., all samples from both monitoring areas). All sampling media for a particular SDG should be from the same pre-cleaned laboratory batch. It will be the laboratory's responsibility to notify the PCL immediately if SDGs are delivered incomplete or if shipping problems occurred. If such occurs, the PCL will investigate, resolve the issue, and communicate the resolution to the laboratory and AQSB and District staff.

If any significant problems arise during the sampling period that cannot be resolved by the operator and their management, the PCL will be notified to resolve the issues.

5.3 LABORATORY PROGRAM

The OPAS PCL will act as the laboratory contract manager. Unless otherwise specified, the contract laboratory shall be:

AXYS Analytical Services, Ltd.
2045 Mills Road West
Sidney, British Columbia, Canada V8L358
Attention: M. Coreen Hamilton, Ph.D.
(250) 655-5800

The laboratory will prepare and follow a standard operating procedure (SOP), approved by ARB, which is based on U.S. EPA Methods TO-9A, 1613b and 1668A. [15, 16] The analytical laboratory SOP, generated by the contract laboratory and used for the CADAMP, is confidential, but has been reviewed and approved by OPAS. Section 9.0 of this QAPP outlines the critical quality control aspects of the laboratory procedures.

5.4 SCHEDULE FOR SAMPLING PROGRAM

Preliminary sampling schedules for the Bay Area and South Coast AQMDs are listed in Table 2 and Table 3, respectively. Also, the monthly schedule for sampling and field blank collection for CADAMP can be found at: www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm.

For each sampling period there should be from 11 to 13 samples submitted for analysis to the laboratory. For the first calendar year of monitoring (2002), approximately 129 samples, including field blanks, will be collected.

For each sampling period the laboratory should receive samples as listed below:

- 4 TO-9A samples from SCAQMD (1 cartridge and 4 QFF each)
- 1 collocated sample from the SCAQMD
- 1 field blank sample from the SCAQMD
- 5 TO-9A samples from the BAAQMD
- 1 collocated sample from the BAAQMD (beginning in January 2003)
- 1 field blank sample from the BAAQMD

Sampling will be performed simultaneously at each CADAMP station to the extent feasible. One day per week is scheduled for filter replacement. Otherwise, the samplers will run continuously. The schedule will produce a comprehensive picture of monthly and seasonal concentrations and enhance the spatial representativeness of the data by incorporating a range of wind directions and dispersion scenarios. The nearly continuous sampling schedule will capture emissions from multiple emission sources, incorporate emissions from seasonal operations, and ensure emissions that result from atypical or intermittent facilities' operations are represented in the samples.

5.5 METEOROLOGICAL MEASUREMENTS

Meteorological data (wind speed and direction, temperature, barometric pressure and relative humidity), when available, will be collected by the AQMDs or the AQSB for each site during the sampling period. The meteorological data will be will be stored electronically by the AQMDs or AQSB. The data will be used, when appropriate, to enhance the spatial resolution of the CADAMP results.

6.0 FIELD OPERATIONS

The specific field operating procedures are detailed in the "Field Operation of the California Ambient Dioxin Air Monitoring Program Sampling Network".[17] *www.arb.ca.gov/aaqm/qmosopas/dioxins/field_ops_v1.0.pdf*

Procedures specific to the air sampler are detailed in the "Standard Operating Procedures for Andersen Instruments Poly-Urethane Foam (PUF) Sampler –Special". www.arb.ca.gov/aaqm/qmosopas/dioxins/equipment/puf_sop.pdf

The following section is intended only to summarize the field quality control procedures. Field quality control checks represent those quality control measures necessary to ensure that quality data are generated from the field sampling operations. QA/QC samples that are integral to the field sampling effort include field collocated samples (i.e., field duplicate samples) and field blanks. The quality control samples will be analyzed in the same manner as field samples and will be interspersed with the field samples. The analytical results of these samples will be used to document the validity and assess the quality of data.

6.1 MAINTENANCE OF CADAMP SAMPLERS

Maintenance of the sampling equipment will be performed weekly, monthly and annually as required by and described in the sampler SOP (link to SOP in section 6.0 above). All maintenance performed will be documented.

6.2 INSTRUMENT CALIBRATION AND FREQUENCY

Sampler flow calibration will be performed, as described in the SOP, using a certified and calibrated Orifice Transfer Standard. Each sampler will be calibrated when new and twice annually at a minimum. In addition, each sampler must be calibrated (1) after major repairs or maintenance, (2) whenever any audit point or QC flow check deviates by more than ±10%, and (3) when a different sample collection media (other than that for which the sampler was originally calibrated) will be used for sampling. The multi-point calibration should follow the procedures outlined in the sampler SOP. The appropriate form, identified in the SOP, will be completed for each multi-point calibration. The resulting correlation coefficient (R) must be greater than or equal to 0.9800 and the individual calibration points, as measured with the transfer standard, can not deviate more than 7% from the corresponding values calculated from the calibration linear regression.

6.3 FLOW CHECKS

With the use of brushless motors as included with the Andersen samplers, calibrations must be performed twice annually. (The NDAMN protocol requires calibrations before and after each sampling event). However, single point QC flow checks must be

performed before each sampling event using a certified and calibrated Orifice Transfer Standard. The sampler flow rate is checked on the first day of each 28-day period (day-1 flow check) using the calibrated orifice transfer standard. This check is conducted with the sample PUF/XAD/PUF cartridge in place, but using a dummy QFF and gaskets to eliminate the possibility of contamination of the sample QFF and gaskets. The sampler is adjusted to the Magnehelic set-point and the flow rate is measured with the transfer standard. If the QC flow check result deviates from 240 slpm by more than ±10%, then the sampler must be re-calibrated before further sampling is conducted. Sampling flow rate must be checked and recorded prior to QFF harvest on the inactive sampling days using the Magnehelic gauge installed on the sampler. All QC flow check data will be recorded on the appropriate form identified in the Field Operation document.

6.4 FIELD COLLOCATED SAMPLES

Field collocated samples provide data necessary to evaluate variability resulting from sampling procedures and from any non-homogeneity of the sample matrix. The collocated samples are collected using two identical samplers at the same site, positioned at least two but not more than four meters apart, operated during the same sampling period and under the same sampling conditions. A collocated sampler will be operated for each of the sampling periods at one site in the BAAQMD and at one site in the SCAQMD (Boyle Heights). The collocated sampler at the Oakland site was not installed/operated in 2002.

6.5 FIELD BLANK SAMPLES

Field blanks will be prepared and sent to sampling sites on a rotating basis. One field blank will be collected, submitted and analyzed from each monitoring region for each sampling period. They will also be collected as necessary to evaluate matrix effects on the analysis and to evaluate suspected sample contamination. Field blank media will be sent by the contract laboratory, according to a schedule supplied by the ARB, to the sampling site shipping locations along with the standard CADAMP sampling media. Field blanks (FB) provide data for evaluating contamination introduced into the samples from field activities. Field blanks will be part of every sampling period and each should consist of four QFFs and one PUF/XAD/PUF cartridge. The blank media will be prepared identical to the samples, including addition of the appropriate levels of field spikes.

At the start of the sampling period the cartridge blank and one QFF blank will be briefly inserted into the sampler (no air sampled). After installation, the initial QFF blank is removed and placed in a glass petri-dish on the sampler shelf with the lid off. The cartridge blank is removed and placed inside a glass jar, which is also kept on the shelf of the sampler with its lid off. The lid of the cartridge blank jar remains off during installation of the sample QFF and sample PUF/XAD/PUF cartridge. When the sampler start-up is completed, the lids for the cartridge blank jar and the blank QFF petri dish are replaced. The QFF blank is collected, labeled and stored in the freezer according to the normal procedure. The cartridge blank remains on the sampler shelf throughout the

duration of the sampling period. The lid to the blank cartridge jar is removed only during the interim and final sample collection times. The second, third, and fourth week QFF blanks will be collected at the field sites during sample QFF recovery. All field blank samples will be returned to the contract laboratory along with the ambient samples. The analytical results generated for the field blanks used at each station will be examined. Optimally, no values over the detection limits should be encountered on the field blanks.

Refer to the Field Operation document for specific field blank collection procedures. These procedures are consistent with those used by the U.S. EPA NDAMN program.

6.6 TRIP BLANK SAMPLES

Trip blanks are samples used to assess any contribution to contamination via shipping procedures. A trip blank will consist of the PUF/XAD/PUF cartridge and filter prepared exactly as if intended to be used as field sample media. It is cleaned, spiked, packaged and shipped to the site with the other traps. The trip blank is not exposed, but is returned with the sampled traps/filters and is analyzed with the sample delivery group. Trip blank samples will <u>only</u> be collected and analyzed, at the direction of the PCL, if field blank contamination problems are observed.

6.7 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Custody documentation will be used to track in detail the sample routing, provide consistent sample identification, and record the time spent at or between the origin and destination. These procedures are useful to safeguard against data loss and produce records that can be used to investigate contamination and other potential problems. ARB will maintain standard chain-of-custody (COC) and labeling procedures for each sample as it is collected. The lab will return the original completed COC documentation with the final report. Refer to the Field Operation document for the COC form.

Chain-of-custody documentation includes shipping, sample identification, temperature record, and receipt information. Sample custody seals (signed and dated) will be placed on each sample container following pre-spike of all PUFs by the laboratory, and before the site operator returns the QFFs and PUFs to the laboratory. Each petri dish containing a QFF and each bubble-wrapped PUF cartridge will be secured with sample custody seals (signed and dated) to verify there was no unauthorized tampering with samples after collection and before analysis. Normally, custody seals are placed on the outside of the cooler or ice chest, but in this case U.S. Customs may need to inspect the contents of the coolers so the seals are placed directly on the samples.

Sample tracking begins with preparation and shipping of the sampling media from the contract laboratory to the sampling personnel. The COC will be: 1) sent by the contract laboratory, with the pre-cleaned sampling media, to the site operators, 2) partially completed at the end of the sampling period, signed by the on-site operator, and returned to the contract laboratory with the exposed samples, and 3) fully completed and signed by the contract laboratory. The COC record will indicate the condition and

temperature upon receipt of the samples at the laboratory and a copy of the COC will be returned to the PCL with the analysis reports. All documentation will be written in permanent blue or black ink. In-house chain of custody will be maintained by the laboratory to track movement of samples throughout the laboratory including disposal or return of samples.

All samples will be packaged and labeled for shipping in compliance with current International Air Transport Association (IATA) dangerous goods regulations.

6.8 TRAINING

Each site operator must have experience and/or training in the specific ambient sampling device for measurements of PCDD/F. This experience and/or training should cover operation and maintenance of the Andersen sampler, calibration and quality control procedures, handling of QFF and PUF/XAD/PUF air samples for PCDD/F analysis, sample chain-of-custody (COC), and records documentation. QMB and AQMD staff will train any new operators.

Table 2 CADAMP Monitoring Schedule

San Francisco Bay Area

(Period)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Start Date	12/20 2001	1/17 2002	2/14 2002	3/14 2002	4/11 2002	5/9 2002	6/6 2002	7/4 2002	8/1 2002	8/29 2002	9/26 2002	10/24 2002	11/21 2002	12/19 2002
Sample Type	**Number of Samples per Period**													
Field Samples	5	5	5	5	4	4	4	4	4	4	5	5	5	5
Site Field Blanks	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Collocated Sample	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PERIOD TOTAL	6	6	6	6	5	5	5	5	5	5	6	6	6	6

See complete sampling schedule for 2002.
See complete sampling schedule for 2003.

Table 3 CADAMP Monitoring Schedule

Los Angeles Area

Period	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Start Date	12/20 2001	1/17 2002	2/14 2002	3/14 2002	4/11 2002	5/9 2002	6/6 2002	7/4 2002	8/1 2002	8/29/ 2002	9/26 2002	10/24 2002	11/21 2002	12/19 2002
Sample Type	**Number of Samples per Period**													
Field Samples	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Site Field Blanks	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Collocated Sample	0	0	0	1	1	1	1	1	1	1	1	1	1	1
PERIOD TOTAL	5	5	5	6	6	6	6	6	6	6	6	6	6	6

See complete sampling schedule for 2002.
See complete sampling schedule for 2003.

7.0 LABORATORY OPERATIONS

This section is intended only to summarize the key aspects of the laboratory quality control procedures and criteria and the data deliverables. The contract laboratory Standard Operating Procedures are on file and are considered confidential business material. However, the procedures are derived from U.S. EPA Methods TO9A, 1613B and 1668A. See Figure 5 for a flowchart of the extraction and spiking procedures. Quantifiable data quality objectives (DQOs) and corrective actions for the laboratory work in this study are summarized in Tables 4 and 5. These performance targets are derived from methods TO9A and 1668A. Meeting the DQOs will ensure that the data obtained are of sufficient quality to meet the overall project objectives. Corrective actions, such as reanalysis, will be taken when necessary.

7.1 CERTIFICATION OF QFF AND PUF/XAD

Background levels in the PUF and QFF must be reduced sufficiently to achieve required detection limits. Cleaning procedures are described in Method TO-9A section 10.2.4. Additional cleanup procedures may be necessary to achieve detection limits below those stated in Table 6. Cartridges with PUF and QFF are considered clean for up to 30 days from date of certification when stored in sealed containers. PUF and QFF sampling media will only be used if contamination analysis demonstrates that the detection levels listed in Table 6 are met for all compounds.

7.2 SAMPLE HOLD TIMES

Samples must be stored under blue ice or refrigerated at less than or equal to 4° C. Extraction must be performed within seven days of sampling and analysis performed within 40 days after extraction. Extraction and analysis hold times may be extended for up to one year if samples are maintained at $<-10^{o}$C (QAPP, DEI:NDAMN Section 6.5).[18]

7.3 CALIBRATIONS/CHECK SAMPLES

Solutions containing $^{13}C_{12}$-labeled and unlabeled PCDDs, PCDFs, and PCBs at known concentrations are used to calibrate the instrument. A five point initial calibration is required before any samples are analyzed. Initial calibration is also required if any routine calibration does not meet the required criteria. An additional low calibration point, below those specified in the methods, will be required for quantitation to meet the low detection limits needed in this program. Single point routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks. A routine calibration is also required at the end of a 12-hour shift.

7.4 LABORATORY CONTROL SAMPLES

Laboratory control samples (LCS) are a pair of identically spiked (labeled and unlabeled) QC standards to measure analytical precision and accuracy. A pair of LCS are extracted and analyzed with each batch of samples, termed a sample delivery group (SDG). The blank sample media (PUF and QFF) to be spiked, extracted and analyzed must be from the same batch as the SDG.

7.5 METHOD BLANKS

Method blanks (MB) will be retained by the contract laboratory, and are a measure of the background contributions from glassware, extraction and cleanup solvents and sample matrix. The MB is treated in exactly the same manner as the test samples. The MB should be free of interferences that affect the identification and quantification of target compounds. A valid MB is an analysis in which all internal standard signals are characterized by signal-to-noise ratio greater than 10:1 and the detection limits are adequate for the study. If a valid method blank cannot be achieved, the set of samples must be re-analyzed using the appropriate archived sample extract. If a valid method blank cannot be achieved upon analysis of the archived extract, the sample set will be evaluated on a case-by-case basis using other measurements of contamination control (i.e., field blanks). If problematic background levels exist, the sample or set of samples may be considered unusable.

7.6 INTERNAL STANDARDS

Internal standards are isotopically-labeled analogs that are added to all samples, including method blanks, field blanks and quality control samples, before extraction. They are used along with response factors to measure the concentration of the analytes. The required internal standards are listed in Table 7.

7.7 FIELD STANDARDS

Isotopically-labeled analogs of a known concentration are added to the PUF in the laboratory prior to sampling to determine collection and recovery efficiency of the method. The required surrogate standards are listed in Table 7. For this program, the laboratory will have the responsibility of adding field surrogate standards to the PUF prior to shipping to the field (refer to Section 8.5 on field spikes). The list of field standards was expanded for the CADAMP relative to Methods TO-9A and 1668A.

7.8 CLEAN-UP STANDARDS

A known amount of an isotopically-labeled analog is added to the sample before the clean-up procedures to estimate the clean-up recoveries. Refer to Table 7.

7.9 RECOVERY STANDARDS

A known amount of isotopically-labeled analogs are added to the sample immediately before injection of the extract to estimate the overall recovery of the internal standards. The required recovery standards are listed in Table 7.

7.10 CERTIFIED STANDARDS

Standard solutions used for quantitative purposes should be assayed periodically (i.e., every 6 periods) to assure that the composition and concentrations have not changed. Standard Reference Materials (SRM) containing known concentrations of target compounds may be obtained from the National Institute of Standards and Technology (NIST) or certified reference materials from a source that will attest to the authenticity and concentration may be used. Stock solutions must be traceable to one of these sources. [19]

7.11 QUALITATIVE/QUANTITATIVE IDENTIFICATION CRITERIA

A target analyte or labeled compound is identified in a standard, blank or sample when all of the method criteria are met. Identification criteria include signal to noise ratios, ion ratios and relative retention times. For specific criteria, refer to Method 1668A sections 16.0 and 17.0 for PCBs and Method TO-9A section 14 for dioxins/furans.

7.12 METHOD DETECTION LIMIT

Method detection limits (MDLs) are determined, as specified in 40 CFR Part 136, Appendix B by performing analyses of seven standard method spikes for all native analytes measured at one to five times the estimated detection limit concentrations. [20] The MDLs are calculated as 3.143 (for seven replicates) times the standard deviation of the measured values. Current MDLs will be included in the data packages supplied by the laboratory.

7.13 SAMPLE SPECIFIC DETECTION LIMITS

The sample specific detection limit (SDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level measured at the retention time of interest. The SDL is calculated for each congener that is not detected. The actual sample detection limits will vary depending on the concentration of the analytes present, the presence of any interference, and the performance of the instrument (i.e., the SDL will vary from one sample to the next for each target analyte). The sample specific detection limits will be included in the data packages supplied by the laboratory.

7.14 SECOND COLUMN CONFIRMATION

Analysis of compounds by chromatography involves the use of separation columns. However, isomer specificity for 2,3,7,8-TCDF cannot be achieved on the DB-5 column used for the analysis of dioxins and furans. Therefore, any sample in which 2,3,7,8-TCDF is identified by analysis on a DB-5 column must have a confirmatory analysis performed on a DB-225, SP-2330, or equivalent GC column. The operating conditions may be adjusted to optimize the analysis on the second GC column, but the GC/MS must meet the mass resolution and calibration specifications of the method.

Isomer specificity for all of the target PCB congeners may not be achieved on the SPB-octyl column. Interferences may also preclude qualitative identification of some PCB congeners. Alternate cleanup procedures and/or an alternate GC column (DB-1 or equivalent) must be employed for congener identification, except for PCB 156 and 157 which cannot be resolved. The operating conditions may be adjusted to optimize the analysis on the second GC column, but the GC/MS must meet the mass resolution and calibration specifications of the method. When co-elutions cannot be resolved by either means, the data will be qualified with an appropriate flag.

7.15 SAMPLE ARCHIVE

The contract laboratory shall keep the archived portion of the sample extracts as well as the concentrated analytical extracts, for one year. Extracts will be in sealed glass vials stored in the dark. The extracts are the property of the ARB, and shall be made available to the ARB upon request. The contract laboratory shall notify the ARB and obtain the ARB's approval before disposal of the extracts.

7.16 REPORTING REQUIREMENTS AND DELIVERABLES

The contract laboratory shall deliver written reports to the ARB upon completion of analysis of each SDG. These reports and the analysis data (data package) shall be delivered no later than 30 calendar days after the laboratory receipt of the complete SDG. In the event that the contract laboratory is unable to meet this reporting requirement, the ARB PCL must be notified, and a new delivery date negotiated. Such extensions shall be restricted. Expedited turnaround time (e.g., 7 or 14 day) may be required on a limited basis. Within 15 days of receipt of the ARB's comments on a report, the contract laboratory shall submit a written revised report that incorporates all reasonable changes and additions requested by ARB. A complete data package on CD-ROM must be delivered to the ARB PCL and will consist of the items listed below.

The contract laboratory shall keep on file, for 24 months after the analysis date, all of the data generated during the analysis of ARB's samples. The contract laboratory shall notify ARB, and obtain ARB's approval before any data are destroyed.

A. Documentation

The data package submitted for data validation will consist of five (5) sections:

1. Case narrative;
2. Chain-of-Custody documentation;
3. Summary of results for environmental samples (including detection limits);
4. Summary of QA/QC results; and
5. Raw data.

B. Case Narrative

The case narrative will be written on laboratory letterhead and the data release will be authorized by the laboratory manager or his/her designee. The case narrative will consist of the following information:

1. ARB's sample identification and the corresponding laboratory identification;
2. Parameters analyzed for each sample
3. Whether the holding times were met or exceeded;
4. Detailed description of all problems encountered;
5. Discussion of possible reasons for any QA/QC sample results outside acceptance limits; and
6. Observations regarding any occurrences which may adversely affect sample integrity or data quality.

C. Chain-of-Custody Documentation

Legible copies of Chain-of-Custody forms for each sample shall be submitted in the data package. The date of receipt and the observed sample condition at the time of receipt must be described on the Chain-of-Custody form. Copies of any internal laboratory tracking documents should be included.

D. Summary of Environmental Sample Results (U.S. EPA Contract Laboratory Program (CLP) Form I Equivalent)

The following information is to be included in the summary of sample results for each environmental sample. The summary form should follow the CLP format if possible, but other formats are acceptable provided that all necessary information is included.

- Form title;
- ARB's sample identification and the corresponding laboratory identification;
- Sample collection date;
- Sample matrix;
- Date of sample (or sub-sample) extraction and quantity of sample subjected to extraction, as applicable;

- Date and time of analysis;
- Identification of the instrument used for analysis;
- Gas Chromatography (GC) column and detector specifications;
- Weight or volume of sample used for analysis/extraction;
- Dilution or concentration factor for the sample;
- Method detection limits (MDL) or sample detection limits;
- Analytical results and associated units; and
- Definitions for any laboratory data qualifiers used.

E. Summary of QA/QC Sample Results

The following QA/QC sample results must be presented on QC summary forms to facilitate data validation and data quality assessment activities. The summaries should follow the CLP format, if possible. Other formats will be acceptable provided that all necessary information is included and the summary is easy to follow.

1. Instrument Calibration (for each instrument used)

a. Initial Calibration (CLP Form VI equivalent)

b. Report the analyte concentrations of the initial calibration standards and the date and time of analysis. List the response factor (RF), the average RF, percent relative standard deviation (%RSD), and retention time (for GC analyses) for each analyte. The initial calibration (IC) report must also include a sample identifier (ID), associated injection volume or quantity of sample analyzed, and the acceptance criteria, such as minimum RF values, and associated maximum %RSD values.

c. Continuing Calibration (CLP Form VI equivalent)

Report the concentration of the calibration standard used for the continuing calibration and for the mid-level standard and the analysis date and time. List the RF, percent difference (%D), and retention time (for GC analyses) for each analyte.

2. Method Blank Analysis (CLP Form IV equivalent)

List the environmental samples and QC analyses associated with each method blank. Report the concentrations of any analytes found in the method blanks.

3. Internal Standard/Surrogate Standard/Cleanup Standard Recoveries (CLP Form II equivalent)

Report the name and concentration of each labeled compound added. List the percent recoveries of all labeled compounds in the samples, method blanks, laboratory control samples and other QC analyses.

4. Laboratory Control Sample Analysis (CLP Form III equivalent)

For precision and accuracy data, one pair of laboratory control samples is required per extraction batch. Report the name and concentration of each spiking compound. Samples are to be spiked with all specified compounds. List the spiked sample results (concentration and %R), percent recovery and the relative percent difference (RPD). The acceptance criteria must also be presented to facilitate evaluation of both spike and duplicate results.

5. Other QC Criteria

GC Retention time windows determination (CLP Form X equivalent)

Report the retention time window for each analyte, for both primary and confirmation analyses. Retention time windows are established by performing 3 analyses of standards for all analytes being measured throughout the course of a 72-hour period. The retention time window is defined as plus or minus 3 times the standard deviation of the absolute retention time. Retention time windows are to be updated daily.

Compound identification

Report the retention times and the concentrations of each analyte detected in the samples for both primary and confirmation analyses.

MDL determination

List the method detection limits. Method detection limits are determined by performing analyses of at least 7 standard method spikes for all analytes measured at 2-5 times the required detection limit concentrations. The method detection limits are calculated as 3.143 times the standard deviation of the measured values. Refer to 40 CFR, Part 136, Appendix B.

Control Charts

Provide control charts with data based on LCS analyses. Include a precision of data statement.

F. Raw Data

This section shall include legible copies of the raw data for the following:

- Environmental samples (arranged in increasing sample number order);
- Mass spectrometer tuning and mass calibration;
- Initial and continuing instrument calibrations;
- QC analyses;
- Sample extraction and clean-up logs; and

- Instrument analysis logs for each instrument used.

The raw data for each analysis shall include the following:

- Chromatograms;
- Enhanced chromatogram of target analytes showing any manual reintegations;
- Quantitation reports; and
- Examples of calculations used to determine final data values from instrument readings, including calculations of detection limits.

Legible copies of the raw data shall be organized systematically, each page shall be numbered, and a table of contents must be included with each package. The raw data for compound identification and quantitation must be sufficient to verify each result presented in Sections 7.16 D and E.

G. Electronic Data Deliverables

Analytical results will be provided electronically in Microsoft Excel format (Office 1997). All documentation, as described in Section 7.16, Reporting Requirements and Deliverables, will be stored on CD-ROM.

Figure 5 Sample Extraction Flowchart

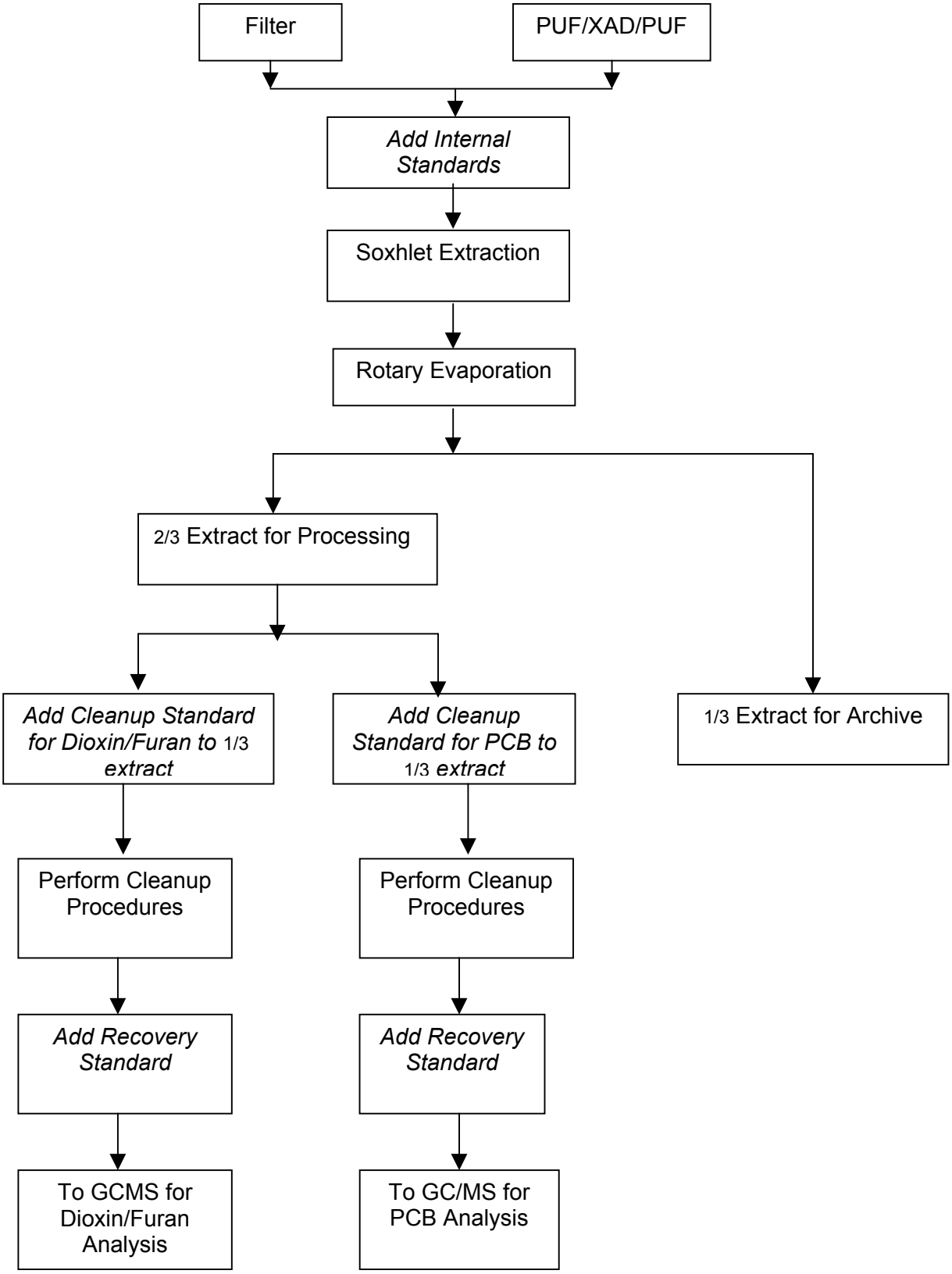


Table 4

Method TO-9A Quality Control Procedures

Method	Quality Parameter	Method/Frequency	Criteria	Corrective Action
TO-9A	Initial Calibration (6 point)	Initially and as required if routine calibration does not meet criteria	Int. Std. RRF<25-30% RSD per method Natives RRF<25-30% RSD per method Surrogates RRF<25% RSD Ion ratios within method Table 19 limits S/N > 10:1 labeled stds. S/N > 5:1 for natives	Terminate analysis. Recalibrate and verify before sample analysis.
	Continuing Calibration Verification (CCV) (*single point CS3*)	Performed prior to sample analysis and at end of 12 hour shift	Int. Std. <25-30 %D per method Natives <25-30 %D per method Surrogates <25 %D Ion ratios within method Table 19 limits S/N > 10:1 labeled stds. S/N > 5:1 for natives	Recalibrate and verify. Reanalyze samples back to last good CCV.
	MS Resolution Demonstration	Prior to ICAL , once per 12 hours, prior to sample analysis	Resolving power ≥ 10,000 (10% valley) at appropriate m/z, ± 5 ppm of expected mass	Retune instrument Reanalyze PFK
	GC Resolution Demonstration	Prior to ICAL, once per 12 hours, prior to sample analysis	Use window defining mix to set retention times Column Performance Check Solution ≤ 25% valley resolution for TCDD and nearest peak	1)Readjust windows 2)Evaluate system. 3)Perform maintenance 4)Reanalyze
	Internal Standards	Add to all calibration standards, every sample, MB, LCS and QC	50 – 120% for tetra-, penta-, hexa-CDD/CDF 40 – 120% for hepta-, octa-CDD/CDF	1)Check chromatogram for interference, if found, perform additional cleanups and reanalyze, flag data 2)Check instrument and reanalyze the extract if a problem is found and corrected 3)Check S/N, if < 10:1,reanalyze 4)Reprocess archived extract 5)Evaluate data useability and flag and narrate as appropriate (reextract is not an option for air samples)

Table 4 (cont.)

Method	Quality Parameter	Method/Frequency	Criteria	Corrective Action
TO-9A	Method Blank	1 per analytical batch, not to exceed 20 samples, per matrix; must be from same matrix clean-up batch as used for samples to be analyzed	S/N > 10:1 labeled stds. Not to exceed DLs in QAPP Table 6	1)Reanalyze method blank 2)If MB still exceeds and analyte conc. in sample < QAPP DLs or > 10X blank conc., report results and flag MB and associated samples 3) If noncompliant and analyte conc. in sample is between QAPP DLs and 10x blank conc., assess source of contamination. Process and analyze archive portion of MB and samples using additional clean-up steps as necessary. 4) If still noncompliant and analyte conc. in sample is between QAPP DLs and 10x blank conc., flag MB and sample results and narrate (reextract is not an option for air samples)
	LCS	1pair per analytical batch, not to exceed 20 samples, per matrix; must be from same matrix clean-up batch as used for samples to be analyzed	70 – 130% native recovery	1)Review Internal Standards, as below 2)Re-run if appropriate 3)If still noncompliant, process and run archive portions 3)If still noncompliant and if sample results are ND and QAPP DLs are met, flag and narrate 4)If samples have positives, flag LCS and samples and narrate (as re-extraction is not an option for air samples)
	Field Standards	Add to every PUF prior to shipping from lab to field and add to every MB and LCS	50 – 120%	1)Check chromatogram for interference If found, perform additional cleanups and reanalyze, flag data. 2)Check instrument and reanalyze the extract if a problem is found and corrected 3)Check S/N, if < 10:1, reanalyze 4)Evaluate data useability and flag as appropriate

Table 4 (cont.)

Method	Quality Parameter	Method/Frequency	Criteria	Corrective Action
TO-9A	Detection Limits	MB and PUF certification (All detection limits are sample specific and congener specific)	Method Blank and PUF certification analysis must not exceed DLs in QAPP Table 6	Reclean and reanalyze PUF as needed See MB criteria above
	Holding Time	All samples	7 days from sampling to extraction or 1 year to extraction if stored at <-10 ^{o}C in dark /40 days from extraction to analysis	Evaluate data for useability Flag samples as appropriate

Table 5

Method 1668A Quality Control Procedures

Method	Quality Parameter	Method/Frequency	Criteria	Corrective Action
1668A	Initial Calibration (6 point)	Initially and as required if routine calibration does not meet criteria	Int. Std. RRF<40% RSD Native RRFs <20% RSD Ion ratios within method Table 8 limits S/N > 10:1 labeled stds. S/N > 5:1 for natives	Terminate analysis. Recalibrate and verify before sample analysis.
	Continuing Calibration Verification (CCV) (single point CS3)	Performed prior to sample analysis and at end of 12 hour shift	Int. Std. <40 %D Natives <30 % Ion ratios within method Table 6 limits S/N > 10:1 labeled stds. S/N > 5:1 for natives	Recalibrate and verify. Reanalyze samples back to last good CCV.
	MS Resolution Demonstration	Prior to ICAL , once per 12 hours, prior to sample analysis	Resolving power ≥ 10,000 (10% valley) at m/z in range of 300 to 350 for significant PFK fragment , ±5 ppm expected mass	Retune instrument. Reanalyze PFK
	GC Resolution Demonstration	Prior to ICAL, once per 12 hours, prior to sample analysis	Use window defining mix to set retention times Column Performance Check Solution ≤ 25% valley resolution for PCB 126 & 169	1)Readjust windows 2)Evaluate system. 3)Perform maintenance 4)Reanalyze
	Internal Standards	Add to every sample, MB and LCS	25 – 150% (see method Table 6)	1)Check chromatogram for interference, if found, perform additional cleanups and reanalyze or reanalyze with alternate column, flag data 2)Check instrument and reanalyze the extract if a problem is found and corrected 3)Check S/N, if < 10:1,reanalyze 4)Reprocess archived extract 5)Evaluate data useability and flag and narrate as appropriate (reextract is not an option for air samples)

Table 5 (cont.)

Method	Quality Parameter	Method/Frequency	Criteria	Corrective Action
1668A	Method Blank	1 per analytical batch, not to exceed 20 samples, per matrix; must be from same matrix clean-up batch as used for samples to be analyzed	S/N > 10:1 labeled stds. Not to exceed DLs in QAPP Table 6	1)Reanalyze method blank 2)If MB still exceeds and analyte conc. in sample < 1 ng or > 10X blank conc., report results and flag MB and associated samples 3) If noncompliant and analyte conc. in sample is between QAPP DLs and 10x blank conc., assess source of contamination. Process and analyze archive portion of MB and samples using additional clean-up steps as necessary. 4) If still noncompliant and analyte conc. in sample is between QAPP DLs and 10x blank conc., flag MB and sample results and narrate (reextract is not an option for air samples)
	LCS	1 pair per analytical batch, not to exceed 20 samples, per matrix; must be from same matrix clean-up batch as used for samples to be analyzed	Natives 50 – 150% Int. Stds. 30 – 140% (see method Table 6)	1)Review Internal Standards, as below 2)Re-run if appropriate 3)If still noncompliant, process and run archive portions 3)If still noncompliant and if sample results are ND and QAPP DLs are met, flag and narrate 4)If samples have positives, flag LCS and samples and narrate (as re-extraction is not an option for air samples)
	Field Standards	Add to every PUF prior to shipping from lab to field and add to every MB and LCS	70 – 130%	1)Check chromatogram for interference If found, perform additional cleanups and reanalyze or reanalyze with alternate column, flag data. 2)Check instrument and reanalyze the extract if a problem is found and corrected 3)Check S/N, if < 10:1, reanalyze 4)Evaluate data useability and flag as appropriate

Table 5 (cont.)

Method	Quality Parameter	Method/Frequency	Criteria	Corrective Action
1668A	Detection Limits	MB and PUF certification (All detection limits are sample specific and congener specific)	Method Blank and PUF certification analysis must not exceed DLs in QAPP Table 6	Reclean and reanalyze PUF as needed See MB criteria above
	Holding Time	All samples	1 year from sampling to extraction/1 year from extraction to analysis stored at <-10°C in dark	Evaluate data for useability Flag samples as appropriate (reextract is not an option for air samples)

Table 6

DETECTION LIMITS [1]

PCDDs/PCDFs	Pg[2]/sample	PCBs	Pg/sample
2,3,7,8-TCDF	3	(77)[3] 3,3',4,4'-TCB	10
1,2,3,7,8-PeCDF	10	(81) 3,4,4',5-TCB	10
2,3,4,7,8-PeCDF	10	(105) 2,3,3;,4,4;-PeCB	50
1,2,3,4,7,8-HxCDF	10	(114) 2,3,4,4',5-PeCB	10
1,2,3,6,7,8-HxCDF	10	(118) 2,3',4,4',5-PeCB	50
1,2,3,7,8,9-HxCDF	10	(123) 2',3,4,4',5-PeCB	10
2,3,4,6,7,8-HxCDF	10	(126) 3,3',4'4',5-PeCB	10
1,2,3,4,6,7,8-HpCDF	15	(156) 2,3,3',4,4',5-HxCB	25
1,2,3,4,7,8,9-HpCDF	15	(157) 2,3,3',4,4',5'-HxCB	25
OCDF	50	(167) 2,3,3',4,4',5-HxCB	25
2,3,7,8-TCDD	3	(169) 3,3',4,4',5,5'-HxCB	10
1,2,3,7,8-PeCDD	10	(170) 2,2',3,3',4,4',5-pHCB	50
1,2,3,4,7,8-HxCDD	10	(180) 2,2'23,4,4',5,5'-HpCB	50
1,2,3,6,7,8-HxCDD	10	(189) 2,3,3',4,4',5,5'-HpCB	10
1,2,3,7,8,9-HxCDD	15		
1,2,3,4,6,7,8-HpCDD	15		
OCDD	50		

(1) Detection limits are based on a single extract that is split for dioxin/furan and PCB analysis, including an archive portion, and assuming a final extract volume of 20 ul. DLs are based on the sample specific detection limit calculation outlined in U.S. EPA Method TO-9A, Section 14.5.
(2) Pg = picograms
(3) (X) indicates IUPAC number

Table 7

LABELLED STANDARDS USED IN THE DETERMINATION OF PCDD, PCDF AND PCB

Time of Addition	Labelled Standards: PCDD/PCDF	Labelled Standards: PCB	PCB IUPAC Number
Before Sampling	**Field Standards**		
	$^{13}Cl_6$-1,2,3,4-TCDD	$^{13}C_{12}$-2,4',5-TriCB	31L
	$^{13}Cl_6$-2,3,7,8-TCDF	$^{13}C_{12}$-2,2',3,5',6-PentaCB	95L
	$^{13}C_{12}$-1,2,3,4,7-PeCDD	$^{13}C_{12}$-2,2',4,4',5,5'-HexaCB	153L
	$^{13}C_{12}$-1,2,3,4,6,7-HxCDD		
	$^{13}C_6$-1,2,3,4,7,8-HxCDF		
	$^{13}C_6$-1,2,3,4,6,7,8-HpCDF		
Before Extraction	**Surrogate Standards**		
	$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-2-MonoCB	1L
	$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-4-MonoCB	3L
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-2,2'-DiCB	4L
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-4,4'-DiCB	15L
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-3,4,4'-TriCB	37L
	$^{13}C_{12}$-OCDD	$^{13}C_{12}$-2,2',6,6'-TetraCB	54L
	$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-3,3',4,4'-TetraCB	77L
	$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-3,4,4',5-TetraCB	81L
	$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,2',4,6,6'-PentaCB	104L
	$^{3}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-2,3,3',4,4'-PentaCB	105L
	$^{3}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,4',5-PentaCB	114L
	$^{3}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-2,3',4,4',5-PentaCB	118L
	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2',3,4,4',5-PentaCB	123L
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-3,3',4,4',5-PentaCB	126L
	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-2,2',4,4',6,6'-HexaCB	155L
		$^{13}C_{12}$-2,3,3',4,4',5-HexaCB	156L
		$^{13}C_{12}$-2,3,3',4,4',5'-HexaCB	157L
		$^{13}C_{12}$-2,3',4,4',5,5'-HexaCB	167L
		$^{13}C_{12}$-3,3',4,4',5,5'-HexaCB	169L
		$^{13}C_{12}$-2,2',3,3',4,4',5-HeptaCB	170L
		$^{13}C_{12}$-2,2',3,4,4',5,5'-HeptaCB	180L
		$^{13}C_{12}$-2,2',3,4',5,6,6'-HeptaCB	188L
		$^{13}C_{12}$-2,3,3',4,4',5,5'-HeptaCB	189L
		$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OctaCB	202L
		$^{13}C_{12}$-2,3,3',4,4',5,5',6-OctaCB	205L
		$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NonaCB	206L
		$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NonaCB	208L
		$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DecaCB	209L
Before Cleanup	**Cleanup Standards**		
	$^{37}C_4$-2,3,7,8-TCDD	$^{13}C_{12}$-2,4,4'-TriCB	28L
		$^{13}C_{12}$-2,3,3',5,5'-PentaCB	111L
		$^{13}C_{12}$-2,2',3,3'5,5',6-HeptaCB	178L
After Extraction	**Recovery Standards**		
	$^{13}C_{12}$-1,2,3,4-TCDD	$^{13}C_{12}$-2,5-DiCB	9L
		$^{13}C_{12}$-2,2',5,5'-TeCB	52L
		$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L
		$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L
		$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L

8.0 DATA MANAGEMENT

SSD staff will coordinate the database management between the groups involved in the program. OPAS staff shall establish, maintain, and update the hard-copy files. The CADAMP electronic web-based database will be created and maintained by OIS. The database will archive temporal monitoring results and will be used to assess and analyze results. The database will include sampling information (i.e., sample start/stop times, start/stop flow rates, and sample volumes), and analytical results. The data will be stored and reports will be generated for distribution and posting on the CADAMP internet site by SSD.

8.1 DATA TRANSMITTAL

All field sampling data sheets (Field Sample Report Form) will be completed by the on-site (AQMD and ARB) operators and forwarded to OPAS at the same time that each exposed sample is shipped to the laboratory. The PCL will enter the appropriate field data into the database. The original COC form will be completed and shipped to the laboratory along with each sample. The laboratory will forward documentation of sample receipt to OPAS staff within 48 hours of receipt of the final sample in a SDG.

Analytical results will be provided to the PCL by the laboratory in Microsoft Excel electronic format and merged with the field information in the CADAMP database. All analytical results (electronic and hardcopy) from sample analysis (or performance evaluation samples) will be forwarded as a draft report to the PCL within 30 days of receipt of the last sample in the SDG. The laboratory report shall follow the format described under Reporting Requirements and Deliverables, as described in Section 7.16. The PCL will provide any comments on each report within 30 days of receipt. The laboratory will then forward an amended report within 15 days of receipt of ARB's comments.

Laboratory Quality Assurance audit reports will be forwarded to the PCL from the QAS manager. AQSB will forward the Calibration and QC reports to the PCL along with available meteorological data. Ultimately, all raw data generated by CADAMP will be submitted to OPAS for review, assessment, and inclusion in the program database.

8.2 DATA VALIDATION

Field data generated by the on-site operators will be reviewed by OPAS staff upon initial receipt of the Field Sample Report and COC. OPAS staff will ensure that field data sheets are appropriately completed, sampling calculations are correct, and will evaluate the field data based on the target criteria listed below to determine whether or not samples should be analyzed. Samples meeting the field quality control criteria will be assumed to have had a sampling flow rate of 240 slpm for the duration of the elapsed sampling time. (Criteria will be re-established when the samplers are modified with pressure transducers and data loggers replacing the Dickson recorders.)

Laboratory data will be verified and validated by the contract laboratory and OPAS staff using the attached checklist. Any errors, omissions or deficiencies will be brought to the attention of the PCL for immediate correction. Initially, the full data validation of the analytical results will be performed for each sample in each SDG.

8.2.1 Field Data Validation (refer to Figure 6)

Sampler Calibration Criteria

- R $\geq$ 0.9800
- %D from true $\leq$ 7% for all five calibration points
- Set-point verification
- Calibration performed within 6 months of sample collection

Sampling Representativeness Criteria

- Pump operation confirmed (elapsed time meter reading confirmed by the Dickson chart)
- Minimum of two valid filter samples submitted for analysis
- One valid PUF submitted for analysis (air sampling must be coincident with that of the valid filters)
- Volume sampled $\geq$ 4147 m^3 (>50% of expected)

Sampling QC Criteria

- Sampling started within 30 days of PUF prep/pre-spike
- Day-1 flow check completed, recorded and $\leq$ 20% from 240 slpm
- Start/end magnehelic gauge readings $\leq \pm$0.8" H_2O from calibration set point (approximately $\pm$ 20% flow rate)
- Stable flow rate for the duration of each 6-day sampling period (as estimated using the Dickson recorder charts)

Transport Criteria

- Samples at $\leq$ 10° C upon receipt at laboratory
- No broken or contaminated samples

8.2.2 Laboratory Data Validation (refer to APPENDIX C)

Case Narrative

- Matrix Anomalies
- QA/QC Anomalies
- Holding Times
- Observations
- Corrective Actions Performed

Calibration Criteria

- Initial Calibration
- Continuing Calibration

Recovery Criteria

- Field Surrogates
- Laboratory Surrogates
- Cleanup Standards

Laboratory QC Samples

- Method Blank
- Laboratory Control Samples

Deviations from the above criteria will be evaluated on a case by case basis. Based upon the professional judgement of the data reviewer, data not meeting all of the criteria listed above may be considered as quantitatively valid. All such assessments will be documented with detailed comments to be included in the database.

8.3 DATA REDUCTION

The laboratory will report analytical results in units specified by the analytical procedures (pg/sample), using the equations given in the TO-9A analytical procedures and the laboratory SOP. The CADAMP database will convert laboratory results to ambient air concentration units of picograms per cubic meter (pg/m^3) and will calculate the Toxic Equivalency (TEQ) (refer to Section 10).

8.4 DATA STORAGE AND REPORT RELEASE

The official data will be stored and backed-up by the ARB on a secure server. ARB and the Bay Area and South Coast AQMD's will review the data before they are made available to the public.

Figure 6 Field Validation Report

Sampling Moment	Bay Area Sites					
00/00/2002	Oakland	Crockett	Richmond	Livermore	San Jose	Field Blank
Calibration Date						na
R > 0.9800?						na
%D < 7 for all 5 cal points?						na
Mag. Cal Set Point						na
Mag. Cal Set-point/+ 0.4 Range						na
Mag. Cal Set-point/+ 0.8 Range						na
Day 1 Flow Check Reading						na
Day 1 Mag. Reading						na
QA LEVEL						na
MAGNEHELIC READINGS Start/End						
Week 1						na na
Week 2						na na
Week 3						na na
Week 4						na na
QA LEVEL						na
REPRESENTATIVENESS CRITERIA						
Elapsed Time (hours)						
Week 1						na
Week 2						na
Week 3						na
Week 4						na
Total Elapsed Tim (576 hours expected)						na
ETM confirmed by Dickson Chart?						na
Total Sample Volume (8294 m3 expected, 4147 minimum with 2 corresp. filters)						na
Sampling started within 30 days of PUF prep?						
DICKSON CHART (flow rate stable? Cannot exceed 2 chart div for > 6 hours or 24hr of no trace)						
Week 1						na
Week 2						na
Week 3						na
Week 4						na
Qualifier						na
TRANSPORT CRITERIA						
Temp. on receipt < 10°C?						
Broken samples?						
VALID SAMPLE? (yes, no, level 3)						
QUALIFIERS						
IF LEVEL 3, WAS REEVAL DONE?						
REEVAL = VALID OR INVALID						
REEVAL DONE BY /DATE						
SAMPLE QUALITY LEVEL (1,2)						
SAMPLE TO BE ANALYZED?						
COMMENTS						

9.0 DATA QUALITY ASSESSMENT

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 accuracy, precision, representativeness, completeness, and comparability.[19] 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 by OPAS staff on a bi-annual basis.

9.1 PRECISION

Precision is defined as the degree of mutual agreement among individual measurements made under prescribed conditions. Laboratory precision will be estimated as the average relative percent difference (RPD) between the analysis results of laboratory control samples (LCS) spiked with native analytes. A pair of LCS will be analyzed with each analytical batch. Method precision will be estimated as the average RPD between collocated sample pairs (refer to Section 6.4). Method precision may also be estimated from the field spike (surrogate) recoveries.

9.2 ACCURACY

Accuracy is defined as the degree of agreement of a measurement to an accepted reference or true value. Laboratory accuracy will be estimated using the average recovery from analysis results of laboratory control samples (LCS) spiked with native analytes. Laboratory accuracy will also be estimated using performance evaluation samples as described in Section 9.7. Method accuracy will be estimated from field spike (surrogate) recoveries. As described in Section 7.7, all samples are pre-spiked in the laboratory with labeled congeners. Field spike recoveries (every sample spiked) provide an indication of the accuracy of the entire sampling and analysis procedure.

9.3 COMPLETENESS

Completeness is an assessment of the amount of valid data obtained compared to the amount of data expected. Completeness will be assessed on a quarterly and annual basis. The DQO for quarterly completeness will be a minimum of 2 (out of 3) valid sampling periods. Four valid quarters per site are required to meet the annual completeness objective. No two consecutive sampling periods may be invalid for calculating an annual average at a particular site.

9.4 REPRESENTATIVENESS

Representativeness involves sample size, sample volume, and sampling times. The CADAMP ambient samplers will be operated 24 days (576 hours) out of every 28-day period in a calendar year. The percent representativeness can be calculated by using the number of hours the samplers operated producing acceptable data divided by the number of total hours required multiplied by 100. The DQO for representativeness for each sampling period is 50 percent (288 hours). A sampling period should include four filters and a PUF cartridge. However, as few as two complete six-day runs (i.e., two QFFs and one PUF) will be accepted as a valid period as long as the volume of air passed through the valid QFFs and the PUF is the same. The sample volume must be $\geq$4150 m^3 (50%). Only samples meeting this minimum sample volume will be considered as valid and analyzed by the contract laboratory.

9.5 COMPARABILITY

Comparability is defined as the confidence with which one data set can be compared to another. The comparability objective is that all data resulting from sampling and analysis be comparable with other representative measurements, such as those made by the U.S. EPA NDAMN program operating under similar conditions. The use of published sampling and analytical methods and standard reporting units will aid in ensuring comparability of the data. The following performance evaluation samples will be used to assess comparability between the CADAMP and NDAMN programs.

9.5.1 Interlaboratory Comparison

To correlate CADAMP and NDAMN data, an inter-laboratory comparison will be conducted between the ARB contract laboratory and the NDAMN analytical laboratory. The ARB Quality Assurance Section (QAS) shall coordinate the inter-laboratory comparison and evaluate and report the results. The comparison will involve the analysis of performance evaluation samples as described in Section 9.7. The comparison will also involve the analysis of matrix blank samples to evaluate detection limits and background contamination problems.

9.5.2 Parallel Sampling

Parallel sampling will involve the collection of side-by-side samples using CADAMP and NDAMN samplers followed by sample analysis by the respective laboratories. Thus, results of the parallel samples will provide a true comparison of the overall sampling and analytical methods. The ARB Quality Assurance Section (QAS) shall coordinate the parrallel sampling comparison and evaluate and report the results.

9.6 DETECTION LIMITS

The field samplers will be operated continuously at 0.24 cubic meters per minute (m^3/min) to obtain a large sample volume (~8300 m^3). Analysis will be performed using

high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) to obtain low method detection limits (approximately 5 picograms (pg)/sample TCDD) to achieve a level of detection in ambient air of approximately 0.6 femtogram (fg)/m^3. If results are reported as less than detection limit then the data will be evaluated to determine if acceptable detection limits were obtained. The effect of any contamination observed in field blanks must be considered. A data qualifier will identify results for which acceptable detection limits were not achieved.

9.7 LABORATORY SYSTEM AND PERFORMANCE AUDITS

Additional quality assurance (QA) shall consist of laboratory system and performance audits. The ARB Quality Assurance Section (QAS) shall coordinate the system and performance audits and evaluate and report the results. System audits of the contract laboratory shall include: (1) facility inspection; (2) personnel qualifications; (3) laboratory certification for HRGC/HRMS analytical methods; (4) SOP and QAPP review; and (5) method detection limit validation (method validation documentation). The laboratory performance audit will consist of the following.

(1) Initial Performance Evaluation Sample (PES)(beginning of program);
(2) Continuing PES (middle of program); and
(3) Final PES (end of program).

The PES will consist of a known concentration of PCDD/PCDF and PCBs to be spiked onto a PUF and sent to the CADAMP contract laboratory for extraction and analysis. The quantitative standards used to generate the PES should be traceable to the National Institute of Standards and Technology (NIST). The PUF will be handled by the contract laboratory as a normal sample and analyzed according to the laboratory's standard operating procedures. The results shall be evaluated by the QAS and a report shall be submitted to OPAS and entered into the CADAMP database. The PES will provide a measure of precision, accuracy and comparability of laboratory performance.

9.8 FIELD SYSTEM AND PERFORMANCE AUDITS

The ARB Quality Assurance Section (QAS) shall coordinate and conduct the field system and sampler flow rate audits and evaluate and report the results to OPAS.

9.9 DATA USABILITY

Data usability is the determination of whether or not a data set is sufficiently complete and of sufficient quality to support the monitoring objective.[21] The assessment of data usability is accomplished upon the completion of a data collection activity by evaluating the documented information against established criteria. A statement on the usability of the data will be included in reports in order to provide data users with adequate information to support their decisions. The usability indicators and criteria described in the above Sections are summarized in Table 8.

Table 8

Data Usability Indicators

Indicator	Criteria
Method Precision	Values reported – No criteria
Method Accuracy (recovery) TO-9A	50 – 120%
Method Accuracy (recovery) 1668A	70 – 130%
Completeness	2 months/quarter, 4 quarters/year
Representativeness	50% sample volume/sampling period
Detection Limits	See Table 6 for target DLs
Performance Evaluation Samples	(TBD)

10.0 REPORTS

The OPAS will generate bi-annual quality control reports. The reports will assess CADAMP's ability to meet the data quality objectives and will provide an expression of the usability of the data. The reports will be reviewed by SSD and the participating districts.

For dioxins and furans, Toxic Equivalence (TEQ) will be calculated and reported by multiplying the concentration of each congener, expressed as pg/m^3, by the associated Toxic Equivalency Factor (TEF) from the Cal/EPA's Office of Environmental Health Hazard Assessment (OEHHA) approved TEF value list (Table 9)(I-TEFs from U.S. EPA 1989).[20] As OEHHA adopts any new TEFs, those new values will be reflected in the TEQ.

Currently, OEHHA has not adopted TEFs for dioxin-like PCBs. In the future, if OEHHA adopts TEFs for dioxin-like PCBs, those TEFs will be incorporated into the TEQ. At this time, an OEHHA unit risk factor will be applied to PCB concentrations to calculate risk.

Table 9
Toxic Equivalency Factors[20]

Compound	Toxic Equivalency Factor
DIOXINS	
2,3,7,8-TCDD	1.0
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
1,2,3,4,6,7,8,9-OCDD	0.001
FURANS	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
1,2,3,4,6,7,8,9-OCDF	0.001

Table 9A

Toxic Equivalency Factors

Coumpound	IUPAC	WHO-97 Toxic Equivalency Factor
DIOXINS		
2,3,7,8-TCDD		1
1,2,3,7,8-PeCDD		1
1,2,3,4,7,8-HxCDD		0.1
1,2,3,6,7,8-HxCDD		0.1
1,2,3,7,8,9-HxCDD		0.1
1,2,3,4,6,7,8-HpCDD		0.01
OCDD		0.0001
FURANS		
2,3,7,8-TCDF		0.1
1,2,3,7,8-PeCDF		0.05
2,3,4,7,8-PeCDF		0.5
1,2,3,4,7,8-HxCDF		0.1
1,2,3,6,7,8-HxCDF		0.1
1,2,3,7,8,9-HxCDF		0.1
2,3,4,6,7,8-HxCDF		0.1
1,2,3,4,6,7,8-HpCDF		0.01
1,2,3,4,7,8,9-HpCDF		0.01
OCDF		0.0001
PCBs		
3,3',4,4' - TeCB	77	0.0001
3,4,4',5 - TeCB	81	0.0001
2,3,3',4,4' - PeCB	105	0.0001
2,3,4,4',5 - PeCB	114	0.0005
2,3',4,4',5 - PeCB	118	0.0001
2',3,4,4',5 - PeCB	123	0.0001
3,3',4,4',5 - PeCB	126	0.1
2,3,3',4,4',5 - HxCB	156	0.0005
2,3,3',4,4',5' - HxCB	157	0.0005
2,3',4,4',5,5' - HxCB	167	0.00001
3,3',4,4',5,5' - HxCB	169	0.01
2,3,3',4,4',5,5' - HpCB	189	0.0001

Please note that OEHHA adopted the WHO-97 TEFs on 08/29/03. All results for the CADAMP network reported as TEQ use these factors. For more information go to http://www.oehha.ca.gov/air/hot_spots/tefs082903.html.

11.0 REFERENCES

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2. U.S. EPA Draft Dioxin Reassessment, "Exposure and Human Health Reassment of 2,3,7,8-Tetrachlorinated dibenzo-p-dioxin (TCDD) and Related Compounds", U.S. EPA Office of Research and Development, 2000, EPA/600/6-88/005Ca

3. Office of Environmental Health Hazard Assessment (OEHHA), "Polychlorinated Dibenzo-p-dioxins (PCDDs), Dibenzofurans (PCDFs) and Biphenyls Including: all 2,3,7,8-chlorinated PCDDs and PCDFs and PCBs" Prioritization of Toxic Air Contaminants - Children's Environmental Health Protection Act, Final Draft, September 2001

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6. ENSR Consulting and Engineering "Ambient Concentrations of PCDDs/PCDFs in the South Coast Air Basin". Document Number 1200-005-700 January 1990. Hunt, G., Maisel, B., Hoyt, M.

7. Senate Bill No. 25, Escutia, Environmental Health Protection: Children, October 10, 1999.

8. United States Environmental Protection Agency. “Compendium Method TO-9A: Determination of Polychlorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins And Dibenzofurans In Ambient Air.” Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Second Addition. Cincinnati, OH: U.S. Environmental Protection Agency, Center for Environmental Research Information. EPA/625/R96/010b. 1999.

9. Thermo Andersen, 500 Technology Court, Smyrna, GA 30082, 800-241-6898

10. Abstract - "Long Duration Measurement of PCDDs/PCDFs in Ambient Air - Method Performance Data", Maisel, B.E., Hunt, G.T. ENSR Corporation

11. California Air Resources Board's Standard Operating Procedures for Air Quality Monitoring (Air Monitoring Quality Assurance, Volume II), Section 2

12. Code of Federal Regulations, Title 40, Part 58, Appendix E, Probe Siting Criteria for Ambient Air Quality Monitoring

13. State of California, Air Resources Board Standard Operating Procedures for Air Quality Monitoring , Andersen Instruments Poly-Urethane Foam (PUF) Sampler - Special, Monitoring and Laboratory Division, January 2002

14. Battelle, “Draft General Procedures for Operation of the National Dioxin Air Monitoring Network” Standard Operating Procedures.

15. U.S. EPA Method 1613, Revision B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, October 1994

16. U.S. EPA “Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS”. U.S. EPA Office of Water, EPA No. EPA-821-R-00-002, December 1999.

17. State of California, Air Resources Board Field Operation of the California Ambient Dioxin Air Monitoring Program (CADAMP) Sampling Network, Air Quality Surveillance Branch, Monitoring and Laboratory Division, Quality Management Branch, Monitoring and Laboratory Division, January 10, 2002

18. National Institute of Standards and Technology, Bldg. 227, Rm A141, 100 Bureau Dr., Stop 8392, Gaithersburg, MD 20899-8392

19. Code of Federal Regulations, Title 40, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit

20. I-TEF as described in Air Toxics Hot Spots Program Risk Assessment Guidelines, Part II, Technical Support Document for Describing Available Cancer Potency Factors (April 1999, California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Table 2, pg. 559)

21. Fairless, Billy J., Ph.D., Bates, Dale I., “Estimating the Quality of Environmental Data,” Pollution Engineering, March 1989, pgs. 108 – 111.

APPENDIX A

ROLES AND RESPONSIBILITIES
BAY AREA AIR QUALITY MANAGEMENT DISTRICT

August 14, 2001

Mr. Gary Kendall
Technical Services Division
Bay Area Air Quality Management District
939 Ellis Street
San Francisco, CA 94109

Dear Mr. Kendall:

The following roles and responsibilities of the Air Resources Board and Bay Area Air Quality Management District, as agreed by our staffs, are in support of the two SB25 Children's Health sites and the five dioxin sites.

Oakland-Fruitvale and Crockett SB25 Sites

ARB Responsibilities

- Install and remove mobile air monitoring stations, including site development and utilities.
- Purchase and acceptance test PUF Dioxin samplers.
- Install, operate and maintain the following air pollution monitoring equipment:
  - API 400 Ozone analyzers
  - API 200 or Teco 42 NOx analyzers
  - DASIBI 3008 CO analyzers
  - Teco 43 SO2 analyzers
  - BAM 1020 PM2.5 analyzers
  - Magee Scientific Aethalometers
  - All MetOne meteorological sensors and associated electronics
  - ESC 8800, ESC8816 or EMC System Manager Dataloggers
  - Environics 9100 gas calibration systems
- Install and maintain the following air pollution monitoring samplers:
  - Xontech 910A canister samplers
  - Xontech 920 multimedia samplers
  - PM10 SSI Samplers
  - PUF Dioxin Samplers
    - 2 samplers at Fruitvale (1 TO9, 1 Low LOD TO9)
    - 1 sampler at Crockett (TO9)
- Perform pre and post calibration of sampling equipment.
- Perform required span, zero, flow and leak checks on samplers and analyzers.
- Conduct annual performance audits on compatible sampling equipment.
- Provide adequate supply of sampling media.

- Perform laboratory sample analysis.
- Perform monthly data review and submittal of data to AIRS.
- Complete all sampler maintenance documentation (monthly QC sheets)
- Provide Standard Operating Procedures (SOP) and operational training for PUF sampler.
- Perform twice yearly calibration of PUF samplers.
- Poll, edit, and report data to AIRS.

BAAQMD Responsibilities

- Operate, load, and unload sampling media in the following air samplers:
  - Xontech 920 sampler on a 1 in 6 day sampling schedule
  - Xontech 910 sampler on a 1 in 6 day sampling schedule
  - PM10 SSI sampler on a 1 in 6 day sampling schedule
  - PUF sampler on a once a month sampling schedule, pre-filter to be changed out on a 1 in 6 day sampling schedule
- Coordinate with ARB to ensure adequate supply of sampling media
- Collect and forward sampled media to ARB laboratory or designee.
- Complete all records for each sample taken at the site (24-hour sample reports).

For the San Jose 4th Street, Livermore, and Richmond Dioxin Sites

ARB Responsibilities

- Purchase, acceptance test, and install PUF samplers.
  - 2 samplers at San Jose (1 TO-9, 1 Connecticut Sampler)
  - 2 samplers at Livermore (1 TO-9, 1 TO-9 Collocated)
  - 1 sampler at Richmond (TO-9)
- Provide Standard Operating Procedures (SOP) and operational training.
- Provide sampler maintenance.
- Conduct performance audits on PUF samplers.
- Provide adequate supply of sampling media.
- Perform twice-yearly calibration of PUF samplers.

BAAQMD Responsibilities

- Operate, load, and unload the PUF sampler on a once a month sampling schedule, with the pre-filter to be changed out on a 1 in 6 day schedule.
- Coordinate with ARB to ensure adequate supply of sampling media.
- Collect and forward sampled media to the designated laboratory.
- Complete all records for each sample taken.

Mr. Gary Kendall
August 14, 2001
Page 3

The attached calendar shows the SB25 and Dioxin sampling schedules for the period of November, 2001 through April, 2002.

Staff should contact Pat Vaca of the Special Purpose Monitoring Section at (916) 324-1146 for the coordination and shipping of all sampling media, or for questions regarding the sampling sites.

Thank you for your support of this important project and please contact me should you have any questions or comments at (916) 445-3745. I look forward to working with you and your staff in the coming months.

Sincerely,

\s

Kenneth Stroud
Chief, Air Quality Surveillance Branch

Attachment

cc: Bill Loscutoff, MLD
Pat Vaca, MLD
Mark Stoelting, BAAQMD
Avi Okin, BAAQMD

APPENDIX B

ROLES AND RESPONSIBILITIES
SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

November 20, 2001

Mr. Rudy Eden, Senior Enforcement Manager
Lab Services and Special Programs
South Coast Air Quality Management District
21865 Copley Drive
Diamond Bar, CA 91765-4182

Dear Mr. Eden:

Listed below are specific responsibilities of the Air Resources Board and South Coast Air Quality Management District, as agreed, to ensure successful operation of dioxin samplers in the South Coast Air Basin.

As requested, we will provide you with a minimum two week review period of all data collected within the South Coast prior to public release. This review period has been incorporated into our Quality Assurance Program Plan.

For the Reseda and Rubidoux Dioxin Sites

ARB Responsibilities

- Purchase, acceptance test, and install PUF samplers.
- Provide Standard Operating Procedures (SOP) and operational training.
- Provide sampler maintenance.
- Conduct performance audits on PUF samplers.
- Provide adequate supply of sampling media.
- Perform twice-yearly calibration of PUF samplers.

SCAQMD Responsibilities

- Operate, load, and unload the PUF sampler every 28 days, with the pre-filter to be changed out on a 1 in 7 day schedule (every Wednesday).
- Coordinate with ARB to ensure adequate supply of sampling media.
- Collect and forward sampled media to the designated laboratory.
- Complete all records for each sample taken.

Thank you for your support of this important project and please contact me should you have any questions or comments at (916) 445-3745. I look forward to working with you and your staff in the coming weeks.

Sincerely,

\s

Kenneth Stroud
Chief, Air Quality Surveillance Branch

Attachment

cc: Bill Loscutoff, MLD

APPENDIX C

CALIFORNIA AMBIENT DIOXIN AIR MONITORING
LABORATORY DATA VERIFICATION
AND
VALIDATION CHECKLIST

Laboratory Data Verification and Validation Checklist

ITEM	√	COMMENTS
1. CD-ROM		
Summary Report, Raw Data, EDD present		
2. CASE NARRATIVE		
Sample ID/Lab ID		
Analytical Parameters		
Holding Times		
Matrix Anomalies		
QA/QC Anomalies		
Observations		
Corrective Actions Performed		
3. CHAIN OF CUSTODY		
COC present		
Field Documents present		
Lab Internal COC present		
4. RAW DATA (all present?)		
Mass Resolution Check		
Initial Calibration		
Continuing Calibration		
Field Samples		
QC Samples		
Dilution Data		
Sample Extraction and Cleanup Logs		
Instrument Analysis Logs		
Chromatograms		
Enhanced Chros. for Reintegrations		
Quantitation Reports		
Example Calculations		

ITEM	√	COMMENTS
5. FIELD SAMPLE RESULTS		
Sample ID/Lab ID		
Sample Collection Date		
Sample Matrix		
Extraction Date (before analytical date?)		
Sample Quantity Extracted		
Date and Time of Analysis		
Instrument ID		
GC Column ID		
Extract Injection Volume		
Dilution or Concentration Factor		
S/N ≥ 2.5		
Sample Specific DLs		
Analyte Concentrations		
Recoveries		
Internal Standards (tetra – hexaCDD/CDF 50 – 120%, hepta, octaCDD/CDF 40 – 120%)		
S/N ≥ 10 for internal standards		
Alternate Standard (50 – 120%)		
Cleanup Recovery Standard (50–120%)		
Field Surrogates (70 – 130%)		
Units Specified and Correct		
Confirmation Analysis (2,3,7,8-TCDF)		
Date and Time of Confirmation Analysis		
Confirmation Instrument ID		
Confirmation GC Column ID		
Confirmation Extract Injection Volume		
Dilution or Concentration Factor for Confirmation Analysis		
Sample Specific DLs		
Analyte concentrations		
Units Specified and Correct		
Data Qualifiers Defined		

ITEM	√	COMMENTS
6. QA/QC SUMMARY RESULTS		
Mass Resolution Check (10,000/10% valley)		
PFK exact mass 380.9760 verified		
Window Defining Mix (Retention Times for all homologs established)		
Column Performance Standard Mix (25% valley for TCDD)		
Initial Calibration		
Sample ID		
Extract Injection Volume		
Date and Time of Analysis		
5 Concentration levels		
Ion Ratios within Limits		
S/N $\geq$ 10 for internal standards		
S/N $\geq$ 2.5 for target analytes		
Relative Response Factor		
Average Response Factor		
%RSD ($\pm$20% unlabeled, $\pm$30% labeled standards)		
Continuing Calibration		
Sample ID		
Extract Injection Volume		
Date and Time of Analysis		
Performed at beginning and end of 12 hour shift		
Mid-level Standard Analyte Concentrations		
Relative Response Factor within 20% mean value of ICAL for unlabeled and 30% for labeled (%D)		
Ion Ratios within Limits		

ITEM	√	COMMENTS
Method Blank		
Sample ID		
Extraction Date		
Extract Injection Volume		
Date and Time of Analysis		
Associated Field and QC Samples Identified		
MB identified for each extraction batch (1 per 20 field samples)		
Analyte Concentrations and/or Detection Limits below target		
% Recoveries		
Internal Standards (tetra – hexaCDD/CDF 50 – 120%, hepta, octaCDD/CDF 40 – 120%)		
Alternate Standard (50-120%)		
Cleanup Recovery Standard (50-120%)		
Field Surrogates (70-130%)		
Laboratory Control Samples		
Sample ID		
Extraction Date		
Extract Injection Volume		
Date and Time of Analysis		
Associated Field and QC Samples Identified		
LCS pair identified for each extraction batch (1pair per 20 field samples)		
% Recoveries		
Internal Standards (tetra – hexaCDD/CDF 50 – 120%, hepta, octaCDD/CDF 40 – 120%)		
Alternate Standard (50-120%)		
Cleanup Recovery Standard (50-120%)		
Field Surrogates (70 – 130%)		
Amount Spiked		
Spike Recoveries		
RPD Between LCS Pair		

ITEM	√	COMMENTS
Method Detection Limit Study present		
Control Charts present		
Data Precision Statement		
Collocated Samples / Parallell Samples		
RPD ≤ 50%		
Field Blanks		
Analyte concentrations below target DL?		