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THE CALIFORNIA AMBIENT DIOXIN AIR MONITORING PROGRAM (CADAMP): MEASUREMENT OF CDDs, CDFs AND DIOXIN-LIKE PCBs AT NINE URBAN SITES IN CALIFORNIA: DECEMBER 2001 – DECEMBER 2002

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Introduction

The California Air Resources Board (ARB) recently established a comprehensive ambient air quality monitoring and testing program to collect data for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (PCBs). Beginning Summer 2003, monitoring will begin for polybrominated diphenyl ethers (PBDEs) as well. The California Ambient Dioxin Air Monitoring Program (CADAMP) is being conducted in two large urban regions of California over a two-year period. CADAMP is one of three elements of the ARB's dioxin program. The other two elements address source-level measurement of dioxins, furans and dioxin-like PCB emissions from stationary sources and motor vehicles. Stationary source testing is currently underway and will be conducted on approximately ten dioxin-emitting source categories. The focus of this paper is on the ambient CADAMP component.

The specific objectives of CADAMP are:

- To assess airborne concentration of dioxins, furans, and dioxin-like PCBs in populated areas in California potentially impacted by emissions from stationary and mobile sources;
- To use this information to consider the need for further emission reduction strategies and identify areas where additional study may be needed; and
- To provide additional information for the California Children's Environmental Health Protection Act (SB25) monitoring program by using the same sampling sites.

CADAMP is modeled, in part, after the U.S. Environmental Protection Agency's (U.S. EPA) National Dioxin Air Monitoring Network (NDAMN) and uses similar sampling and analytical protocols. CADAMP, however, has an urban focus while the NDAMN program focuses in rural areas to study pathways by which dioxins enter the food chain. Unique to CADAMP is the inclusion of limited ambient sampling for PBDEs.

Methods

CADAMP samples are collected at five urban sites in the San Francisco Bay Area, and four urban sites in the South Coast Air Basin. Monitoring in the Bay Area occurs in San Jose, Oakland, Richmond, Crockett, and Livermore and is done in cooperation with the Bay Area Air Quality Management District. Sites in the South Coast area are in Boyle Heights, Wilmington, Reseda, and Rubidoux and are supported by the South Coast Air Quality Management District. CADAMP began in the Bay Area and South Coast in December 2001 and will continue at least through early

2004. Additional sites were added in Sacramento and San Francisco in January 2003. A contract laboratory specializing in the analyses of dioxins/furans and PCBs analyzes the samples.

CADAMP monitoring compliments the two rural NDAMN monitoring sites in California. The first is a background site on the coast north of San Francisco that represents onshore flow from the Pacific Ocean (Fort Cronkhite). The other NDAMN site is located in an agricultural area approximately 25 miles south of Sacramento at Rancho Seco.

U.S. EPA Method TO-9A is used as the basis for the ambient air sampling and analytical procedures for CADAMP. The sampler collects atmospheric particulate material on a quartz fiber filter (QFF) while vapor-phase constituents pass through the QFF and impinge on a pre-cleaned polyurethane foam plug (PUF) inside a glass cartridge. The samplers are operated in the standard configuration described in Method TO-9A, but the sampling period has been extended to cover an entire month (576 hours - 24 days out of every 28 days). This results in 13 28-day sampling moments per year. The PUF is augmented with XAD-2 resin between two portions of the PUF, forming a PUF-XAD-PUF sandwich. QFFs are replaced weekly to prevent overloading the filter with particulate. The PUF sandwich remains in place for the four weeks of the sampling moment. Over 300 samples will be collected an analyzed for dioxins, furans, and dioxin-like PCBs.

The four QFFs and one PUF sandwich are combined and extracted per U.S. EPA Method TO-9A, as one sample. The single extract is used for analysis of dioxins, furans and 14 dioxin-like PCBs by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Selected samples will be analyzed for 44 PBDE congeners.

The detection limit is approximately 0.2 femtogram per cubic meter (fg/m^3) for 2,3,7,8-TCDD, achieved by using the extended sampling period. The low detection limits are necessary because the concentrations of many of the PCDD, PCDF, and PCB congeners of concern are normally detected in ambient air at very low concentrations. Since non-detects are seldom observed using the extended sampling approach the low detection limits provide for a more accurate determination of toxicity equivalence (TEQ) relative to higher detection limit methods.

A comprehensive plan for field and laboratory quality assurance (QA) was developed for CADAMP that included flow rate verification, collocated and field blank samples, field surrogates, laboratory control samples, and laboratory blanks (and all other performance checks required by Method TO-9a). The QA audit program will include field flow rate and systems audits of each site, a laboratory systems audit, performance evaluation samples submitted to both the contract laboratory and the U.S EPA NDAMN laboratory, and parallel samples collected and submitted to the respective CADAMP and NDAMN laboratories.

Monitoring for PBDEs is expected to begin in 2003 at six of the urban CADAMP monitoring locations (San Jose, Oakland, Richmond, Boyle Heights, Wilmington, and Rubidoux) and is expected to run for one year.

Results

The following are the results for twelve sampling periods under CADAMP (we do not have the data from NDAMN for these sampling periods). Figures 1 and 2 show CADAMP results for the

Bay Area and South Coast. This data, as well as the results presented below are the preliminary results that were available at the time this paper was prepared.

California officially uses the 1989 International Toxic Equivalency Factors (TEFs) at the present time. However, for comparison purposes, the WHO 97 TEF values are used throughout this paper. The WHO 97 TEF values are used in NDAMN and are currently undergoing scientific peer review for use in California. The following concentration results are listed as total toxicity equivalence (TEQ) in femtograms per cubic meter (fg/m^3). The total TEQ represents the sum of the individual TEQs for dioxins, furans and PCBs, per sample.

- In the Bay Area, the TEQs ranged from 7.5 to 191.1 fg/m^3. The lowest TEQ of 7.5 fg/m^3 was during the June 6, 2002, sampling period in Livermore. The highest TEQ of 191.1 fg/m^3 was observed during the January 17, 2002, period at Livermore (Figure 1). Staff is investigating why this TEQ was significantly higher than the other TEQs during this sampling period.
- In the South Coast Air Basin, the TEQs ranged from 10.6 to 167.1 fg/m^3. The lowest TEQ of 10.6 fg/m^3 occurred during the May 16, 2002, sampling period in Wilmington. The highest TEQ of 167.1 fg/m^3 was during the August 29, 2002, period at Reseda (Figure 2). Although we are continuing to investigate, staff's preliminary findings indicate that this TEQ could be attributed to a nearby forest fire.
- In the Bay Area, the PCB contribution to the total TEQ ranged from less than one percent to 58 percent. In the South Coast the range was from three percent to 50 percent.

Due to limited data at the publication of this paper, it is difficult to assess the implications for risk management. However, once an adequate amount of data are available, the ARB will use the ambient concentrations in conjunction with results from stationary source testing to determine where to focus risk management efforts.

Acknowledgements

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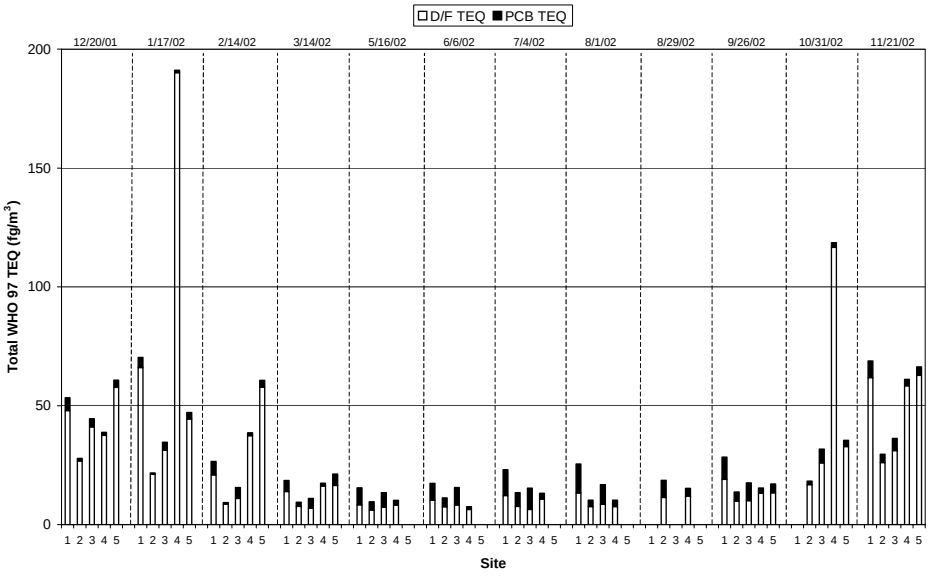
References

Refer to http://www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm for the following CADAMP documents and information:

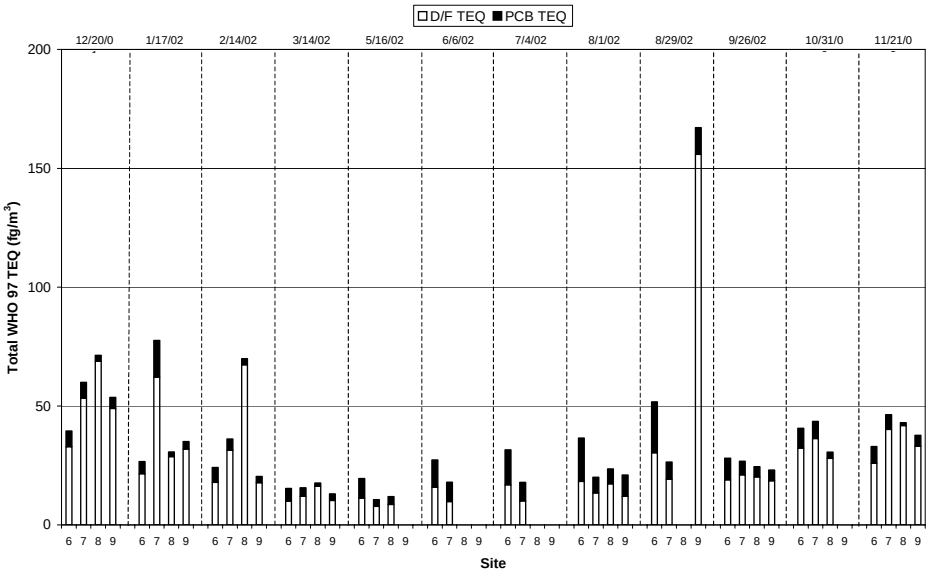
- The California Ambient Dioxin Air Monitoring Program Quality Assurance Project Plan;
- The Field Operation of the California Ambient Dioxin Air Monitoring (CADAMP) Sampling Network;
- The Standard Operating Procedures for Andersen Instruments Poly-Urethane Foam (PUF) Sampler-Special;
- A link to detailed descriptions of the network monitoring sites;
- The sampling schedule; and
- A link to the monitoring results.

Figure 1: CADAMP Results for the San Francisco Bay Area



1-Oakland, 2-Crocket, 3-Richmond, 4-Livermore, 5-San Jose

Figure 2: CADAMP Results for the South Coast Air Basin



6-Boyle Heights, 7-Wilmington, 8-Rubidoux, 9-Reseda