

2005
ANNUAL DATA QUALITY REPORT
AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION

2005

Annual Data Quality Report

for the

Monitoring and Laboratory Division's
and
Local Districts' Air Monitoring Networks

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I. INTRODUCTION

The purpose of this report is to provide ambient air quality data users with a summary of the quality of the 2005 ambient data in quantifiable terms. This is the eighth edition of the report and presents an overview of various quality assurance and quality control activities. The tables included in this report provide summary data for ambient air monitoring stations in the statewide network.

The California Air Resources Board's (ARB) mission is to promote and protect public health, welfare, and ecological resources through effective and efficient reduction of air pollutants while recognizing and considering the effects on the economy of the State. The Monitoring and Laboratory Division (MLD) provides a key element of that mission through collecting and reporting on quality information on a large number of pollutants and for a vast air monitoring network. The MLD, directed by State law, conducts ambient air monitoring in support of ARB, local air pollution control and air quality management districts (Districts), and the United States Environmental Protection Agency (U.S. EPA). Monitoring programs include gaseous criteria and non-criteria pollutants, particulate matter, toxic air contaminants, non-methane hydrocarbons, pesticides, dioxins, meteorological parameters, and visibility. Data from these monitoring sources provide the means to determine the nature of the pollution problem and assess the effectiveness of the control measures and programs. The MLD mission includes supporting the regulatory and assessment programs of the Board.

It is the goal of MLD to provide accurate, relevant, and timely measurements of air pollutants and their precursors to support California's Air Quality Management Program for the protection of public health. The Quality Assurance Section (QAS) conducts various quality assurance activities to ensure that data collected comply with procedures and regulations set forth by the U.S. EPA and can be considered good quality data and data-for-record.

What is quality assurance? Quality assurance is an integrated system of management activities that involves planning, implementing, assessing, and assuring data quality through a process, item, or service that meets users needs for quality, completeness, representativeness and usefulness. Known data quality enables users to make judgments about compliance with air quality standards, air quality trends and health effects based on sound data with a known level of confidence. The objective of quality assurance is to provide accurate and precise data, minimize data loss due to malfunctions, and to assess the validity of the air monitoring data to provide representative and comparable data of known precision and accuracy.



Quality assurance is composed of two activities: quality control and quality assessment. Quality control is composed of a set of internal tasks performed routinely at the instrument level that ensures accurate and precise measured ambient air quality data. Quality control tasks address sample collection, handling, analysis, and reporting. Examples include calibrations, routine service checks, chain-of-custody documentation,

duplicate analyses, development and maintenance of standard operating procedures, and routine preparation of quality control reports.

Quality assessment is a set of external, quantitative tasks that provide certainty that the quality control system is satisfactory and that the stated quantitative programmatic objectives for air quality data are indeed met. Staff independent of data generators performs these external tasks. Tasks include conducting regular performance audits, on-site system audits, interlaboratory comparisons, and periodic evaluations of internal quality control data. Table 1 illustrates the types of performance audits currently performed by ARB for each air monitoring program. Field and laboratory performance audits are the most common. System audits are performed on an as-need basis or by request. Whole air sample comparisons are conducted for the toxic air contaminants and non-methane hydrocarbon programs.

Table 1. Audits Performed for Each Air Monitoring Program in 2005

| Air Monitoring Program | Field Performance Audit | Laboratory Performance Audit | System Audit | Whole Air Audit |
|--------------------------|-------------------------|------------------------------|--------------|-----------------|
| Gaseous Pollutants | X | X | X | |
| Particulate Matter | X | X | X | |
| Toxic Air Contaminants | | X | | X |
| Non-Methane Hydrocarbons | | X | X | X |
| Pesticides | X | | | |
| Dioxin/Furans and PCBs | X | X | | |
| Asbestos | Future | | | |
| Consumer Products | | Future | | |
| Meteorology | X | | X | |

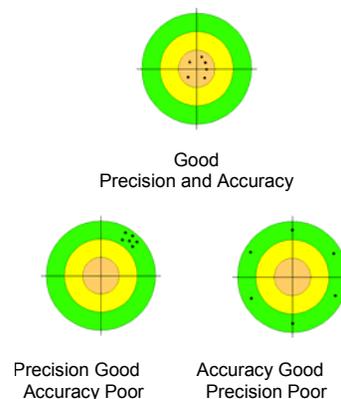
II. QUALITY CONTROL AND QUALITY ASSESSMENT

The QAS supports all ambient monitoring programs undertaken by MLD, which in 2005 includes gaseous pollutants, particulate pollutants, toxic air contaminants, non-methane hydrocarbons, pesticides, dioxin/furans and PCBs and meteorological sensors run by the ARB and local and private air monitoring agencies. There are approximately 260 air monitoring sites in 15 separate air basins operating in California.

Appendix A provides information about the air monitoring network (i.e., sampling schedules, number of instruments, collection/analysis method, etc.). The information in Appendix A is also available at the following Internet site under Air Monitoring Activities at <http://www.arb.ca.gov/aaqm/qmosqual/qmosqual.htm>.

Information about each air monitoring station audited by the ARB is available at <http://www.arb.ca.gov/qaweb/>. The web site includes maps of each site, latitude and longitude coordinates as determined by GPS, site photos, precision and accuracy data, and a detailed survey of the physical parameters and conditions at each site. The site surveys list in-depth monitoring information such as traffic descriptions, calibration dates, distances to trees and obstacles, and residence times. This site also includes an area for District precision and accuracy reports. These reports are available on a limited basis to District staff.

The air quality monitors collect data in both real-time and on a time integrated basis. The data are used to define the nature, extent, and trends of air quality in the State; to support programs required by State and federal laws; and to track progress in attaining air quality standards. The precision and accuracy necessary depends on how the data will be used. The illustration to the right shows the relationship between precision and accuracy. From the figure, it is evident how important having good precision and accuracy is to ensuring good data quality. Data that must meet specific requirements (i.e., criteria pollutants) are referred to as *controlled data sets*. Criteria for the accuracy, precision, completeness, and sensitivity of the measurement in controlled data sets must be met and documented.



Air Quality Data Actions (AQDAs) are a key tool used by QAS to confirm the data set meets the established control limits. They are initiated generally by auditors upon a failed audit and resolved after a review of calibrations, precision checks, and audit results. The AQDA must confirm that an analyzer/sampler has operated within ARB’s control limits of +/-15% (+/-10% for PM10 and +/-4% for PM2.5), or for siting or temperature conditions otherwise, further action is taken.

Data without formal data quality objectives (i.e., toxics) are called descriptive data sets. The data quality measurements are made as accurately as possible in consideration of how the data are being used. Quantified quality assessment results describe the measurement variability in standard terminology, but no effort is made to confine the data set to values within a predetermined quality limit.

The ARB’s Quality Assurance Program is outlined in a six-volume Quality Assurance Manual. The volumes, listed below, guide the operation of the quality assurance programs used by the ARB, local districts, and private industry in California.

- Volume I Quality Assurance Plan
- Volume II Standard Operating Procedures for Air Quality Monitoring
- Volume III Laboratory Standard Operating Procedures
- Volume IV Monitoring Methods for the State Ambient Air Quality Standards
- Volume V Audit Procedures for Air Quality Monitoring
- Volume VI Standard Operating Procedures for Stationary Source Emission Monitoring and Testing

The six-volume Quality Assurance Manual is available on the Internet at <http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.htm>. Volume I lists the data quality objectives and describes quality control and quality assessment activities used to ensure that the data quality objectives are met. Volume II provides guidelines for maintaining and operating air monitoring stations and to provide detailed instructions for testing, maintaining, troubleshooting and calibrating specific analyzers or support equipment. Volume III contains laboratory standard operating procedures (SOP). Volume IV provides the text of the methods that are used to measure air pollutants in

the ambient air in order to determine whether the State ambient air quality standards have been met. Volume V lists the procedures for conducting system and performance audits of the State's air monitoring programs. Volume VI contains SOPs for Stationary Source Emission Monitoring and Testing.

A. Gaseous Pollutants

Ambient concentrations of carbon monoxide (CO), nitrogen dioxide (NO₂), ozone (O₃), sulfur dioxide (SO₂), and hydrogen sulfide (H₂S) are continuously monitored by an automated network of stations run by MLD and the Districts. Exposure to these pollutants cause adverse health effects which include respiratory impairment, fatigue, permanent lung damage, and increased susceptibility to infection in the general population. Gaseous criteria and non-criteria pollutant data are a controlled data set and are subject to meeting mandatory regulations.



Sampling Cane

Accuracy (field): Annually, QAS conducts field through-the-probe (TTP) performance audits for gaseous pollutants to verify the system accuracy of the automated methods and to ensure the integrity of the sampling system.

Accuracy is represented as an average percent difference. The average percent difference is the combined differences from the certified value of all the individual audit points. The upper and lower probability limits represent the expected accuracy of 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site. Audit results were not used in statistical analysis if the audit was invalidated due to an AQDA that resulted in data invalidation.

Overall, the responses of the individual analyzers indicate that as a whole, the network is providing accurate data. Ninety-seven percent of the instruments audited in 2005 were found to be operating within the ARB's control limits (+/-15%). The most common causes for audit failure are malfunctions within the instrument and leaks in the sampling system. Instruments operating outside of ARB's control limits resulted in 118 days of invalidated data. Table A1 summarizes the 2005 performance audit results for the criteria pollutants. Further information about the air monitoring systems and the audit procedures are available at:

http://www.arb.ca.gov/aaqm/qmosqual/sysaudit/criteria/qa_gas.htm.

Table A1. 2005 Results for Criteria Pollutants Performance Audits Conducted by ARB

| Pollutant | Number of Analyzers Audited | Number of AQDAs | Average % Difference | Probability Limits | |
|------------------|-----------------------------|-----------------|----------------------|--------------------|-------|
| | | | | 95%UL | 95%LL |
| CO | 60 | 0 | 0.2 | 6.0 | -5.6 |
| NO ₂ | 79 | 1 | -2.1 | 6.7 | -10.9 |
| O ₃ | 142 | 2 | -0.5 | 5.6 | -6.6 |
| SO ₂ | 21 | 0 | 2.0 | 10.2 | -6.2 |
| H ₂ S | 7 | 0 | 0.8 | 7.7 | -9.3 |

Source: Quality Assurance Section, Accuracy Estimates

Precision (field): Precision checks (zero and span) are performed by site operators on a nightly basis to confirm the linear response of the instrument. The zero precision check confirms the instrument's ability to maintain a stable reading. The span precision check confirms the instrument's ability to respond to a known concentration of gas. The degree of variability in each of these nightly measurements is computed as the precision of that instrument's measurements.

Annually, QAS conducts a precision data analysis as an overall indicator of data quality. The analysis addresses three parameters: precision data submission, precision data validity, and a combination of the two referred to as data usability rates. The precision performance goal for all three parameters is 85%. The submission rate is the number of precision points submitted for a pollutant divided by the expected number of bi-weekly submissions. Data validity is the percent difference of the actual and indicated values of each precision check. These differences should not exceed +/-15% for gaseous analyzers. Usable data rates are determined by multiplying the data submission and data validity rates; and indicate the completeness of verifiable air quality data on the official database. Due to limited resources, QAS was unable to conduct a precision data analysis for 2005.

B. Particulate matter



Particulate matter is a mixture of substances that include elements such as carbon and metals; compounds such as nitrates, organic compounds, and sulfates; and complex mixtures such as diesel exhaust and soil. Particles with an aerodynamic diameter of 10 microns or smaller pose an increased health risk because they can deposit deep in the lung and contain substances that are particularly harmful to human health. Respirable particulate matter (PM10) and fine particulate matter (PM2.5) increase the chance of respiratory disease, lung damage, cancer, and premature death.

Particulate matter monitoring is conducted using both manual and continuous type samplers. Manual samplers are operated on a six-day sampling schedule for PM10, and a similar, or more frequent schedule, for PM2.5. ARB's particulate program also includes total suspended particulates (TSP) sulfate, mass and lead monitoring.



Particulate matter is a controlled data set and as such is subject to formal data quality objectives and federal and state regulations. For additional information about the Particulate Matter Monitoring program, visit the Particulate Matter home page at <http://www.arb.ca.gov/aaqm/partic.htm>.

Particulate Samplers

Accuracy (field): The accuracy of particulate samplers is determined by comparing the instrument's flow rate to a certified orifice (PM10, TSP, and PM2.5 samplers), or a calibrated mass flow meter (TEOM and BAM samplers) that is certified against a National Institute of Standards and Technology (NIST) traceable flow device or calibrator. Since an accurate measurement of particulate matter is dependent upon flow rate, the ARB conducts annual flow rate audits at each site. The average percent difference between the sampler flow rates and the audit flow rates represents the combined differences from the certified value of all the individual audit points for each sampler. The upper and lower probability limits represent the expected flow rate accuracy for 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site. Audit results were not used in the statistical analysis if the audit was invalidated due to an AQDA that resulted in data invalidation. Table B1 summarizes the 2005 performance audit results for the particulate samplers.

Overall, the 2005 flow audit results indicate that the flow rates of samplers in the network are almost all within bounds. Approximately ninety-five percent of the instruments audited in 2005 operated within the ARB's control limits. Instruments operating outside of ARB's control limits resulted in 447 days of invalidated data. The 2005 performance audit results are listed below in Table B1. The TSP data accuracy estimates include samplers that analyze for mass and/or sulfates and/or lead.

Table B1. 2005 Results for Particulate Sampler Performance Audits Conducted by ARB

| Pollutant | Number of Samplers Audited | Number of AQDAs | Average % Difference | Probability Limits | |
|---------------|----------------------------|-----------------|----------------------|--------------------|-------|
| | | | | 95%UL | 95%LL |
| PM2.5 | 96 | 8 | 0.4 | 3.5 | -2.7 |
| PM10 | 119 | 4 | 0.1 | 6.1 | -5.9 |
| PM10 Partisol | 26 | 0 | 0.8 | 4.7 | -3.1 |
| TEOM | 20 | 0 | 0.6 | 5.0 | -3.8 |
| BAM PM10 | 14 | 1 | -0.8 | 4.8 | -6.4 |
| BAM PM2.5 | 47 | 5 | 0.0 | 2.7 | -2.7 |
| TSP | 4 | 0 | -2.7 | 13.1 | -18.5 |

Source: Quality Assurance Section, Accuracy Estimates

Precision (field): Precision data for non-continuous particulate samplers is obtained through collocated sampling whereby two identical samplers are operated side-by-side and the same laboratory conducts filter analyses. Collocated samplers are located at selected sites and are intended to represent overall network precision. Validity of the data is based on the percent difference of the mass concentrations of the two samplers.

Particulate samplers (collocated PM10 and TSP) must have mass concentrations greater than or equal to 20 $\mu\text{g}/\text{m}^3$ to be used in data validity calculations. The difference between the mass concentrations must be no greater than 5 $\mu\text{g}/\text{m}^3$. If the mass concentrations are greater than 80 $\mu\text{g}/\text{m}^3$, the difference must be within +/-7% of each other. TSP (Pb) samplers must have both mass concentrations greater than or equal to 0.15 $\mu\text{g}/\text{m}^3$ to be used in data validity calculations. For collocated PM2.5 samplers, data validity is based on the sampler's coefficient of variation, which cannot exceed 10%. Both sample masses must also be greater than 6 $\mu\text{g}/\text{m}^3$. Continuous TEOM and BAM precision is based on the comparison of the sampler's/analyzer's indicated and actual flow rates. The differences between the flow rates must be within +/-15%. Due to limited resources, QAS was unable to conduct a precision data analysis for 2005.

Accuracy (lab): Annual performance audits for PM10 and PM2.5 mass analysis programs include an on-site check and assessment of the filter weighing balance, relative humidity and temperature sensors, and their documentation. The performance audits conducted in 2005 found that the district programs were operating in accordance with U.S. EPA guidelines and that the data were of good quality and should be considered data-for-record. Table B2 summarizes the performance audit findings.

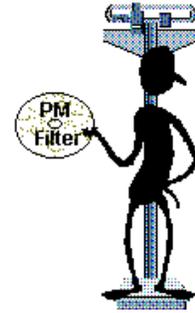


Table B2. 2005 PM10 and PM2.5 Particulate Matter Mass Analysis Performance Audits

| District | Conducted | Pass/Fail |
|---|-----------|-----------|
| California Air Resources Board (PM10 and PM2.5) | 03/30/05 | Pass |
| Bay Area AQMD (PM 2.5 only) | 12/13/05 | Pass |
| Great Basin UAPCD (PM10 and PM2.5) | 09/14/05 | Pass |
| Lake County AQMD (PM10 and PM2.5) | 04/12/05 | Pass |
| Mojave Desert AQMD (PM10 and PM2.5) | 02/10/05 | Pass |
| Monterey Bay Unified APCD (PM10 only) | 04/28/05 | Pass |
| North Coast Unified AQMD (PM10 only) | 06/06/05 | Pass |
| No. Sonoma Co. APCD (PM10 only) | 10/17/05 | Pass |
| Sacramento Metropolitan AQMD (PM10 only) | 12/14/05 | Pass |
| San Luis Obispo Co. APCD (PM10 only) | 04/27/05 | Pass |
| San Diego County APCD (PM 2.5 only) | 08/28/05 | Pass |
| Santa Barbara Co. APCD (PM10 only) | 05/04/05 | Pass |
| Siskiyou Co. APCD (PM10 only) | 06/07/05 | Pass |
| South Coast AQMD (PM 2.5 only) | 12/07/05 | Pass |
| Ventura Co. APCD (PM10 and PM2.5) | 07/21/05 | Pass |

Laboratory audits were also conducted for the PM10 ions program using NIST-traceable filter standards for nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), ammonium (NH_4^+), and potassium (K^+). Audit results for the NLB ions program were within the targeted +/-20% control limit established for the audit procedure. Laboratory audits for the TSP (Pb) program were conducted using NIST-traceable standards. The 2005 audit results for both ions and Pb were found to be within ARB's +/- 20% control limits indicating that NLB is accurately identifying ions and Pb.

Precision (lab): Laboratories perform various quality control tasks to ensure that quality data are produced. Tasks include duplicate weighings on exposed and unexposed filters, replicate analysis on every 10th filter, and a calibration of the balance before each weighing session. Upon receipt of particulate matter filters from the field, laboratory staff have up to 30 days to analyze the PM10 and PM2.5 samples. Filters are visually inspected for pinholes, loose material, poor workmanship, discoloration, non-uniformity, and irregularities, and are equilibrated in a controlled environment for a minimum of 24 hours prior to the filters are weighed. If room conditions are not within the established U.S. EPA control limits, weighings are done only after the proper environment is re-established and maintained for 24 hours.

In 2005, there were no occurrences in which weighings were conducted when ARB's laboratory balance room was outside of control limits. The analytical precision results indicate that ARB is providing precise particulate matter data. Tables B3 and B4 show the unexposed and exposed filter replicate results for ARB's laboratory in 2005.

Table B3. 2005 Summary of ARB's Unexposed Filter Mass Replicates

| QC Checks for Pre-weighed Filters | PM10 | PM2.5 |
|-----------------------------------|------|-------|
| Total # samples analyzed | 4256 | 4206 |
| # of replicates | 532 | 519 |
| % replicated | 12.5 | 12.3 |
| # out-of-range | 0 | 0 |

Source: Inorganics Laboratory Section, Quality Control Report

Table B4. 2005 Summary of ARB's Exposed Filter Mass Replicates

| QC Checks for Post-weighed Filters | PM10 | PM2.5 |
|------------------------------------|------|-------|
| Total # samples analyzed | 4130 | 3512 |
| # of replicates | 465 | 414 |
| % replicated | 11.3 | 11.8 |
| # out-of-range | 0 | 0 |

Source: Inorganics Laboratory Section, Quality Control Report

C. Toxic Air Contaminants

In 1985, ARB established an ambient volatile organic compound (VOC) toxic monitoring network in major urban areas of the state to determine the average annual concentrations of toxic air contaminants (TAC). The program was established to assess the effectiveness of control measures in reducing air toxics exposures. Compounds identified as TACs vaporize at ambient temperatures, play a critical role in the formation of ozone, and have adverse chronic and acute health effects. Sources of TACs include motor vehicle exhaust, waste burning, gasoline marketing, industrial and consumer products, pesticides, industrial processes, degreasing operations, pharmaceutical manufacturing, and dry cleaning operations.



Stainless Steel Toxics Canister

Under the current ARB sampling schedule, ambient air is collected in a stainless steel canister (or cartridge) every 12 days over a 24 hour sampling period at each of the network stations. Toxic particulate samples are also collected and analyzed for toxic air contaminants to support the California Toxic Air Contaminant Identification and Control program. By using a low-flow multi-channel sampler capable of sampling onto filters or cartridges, ambient air is collected and analyzed for carbonyl and polycyclic aromatic hydrocarbons (PAH) compounds and toxic metals. The quality of the air toxic data set is governed by a series of quality assurance activities, including audits. However, because this is a descriptive data set, no mandatory corrections are made to the data

based on audit results. The laboratory and monitoring staff are made aware of any exceedance found during an audit, and every effort is made to ensure that the data collected is as accurate as possible.

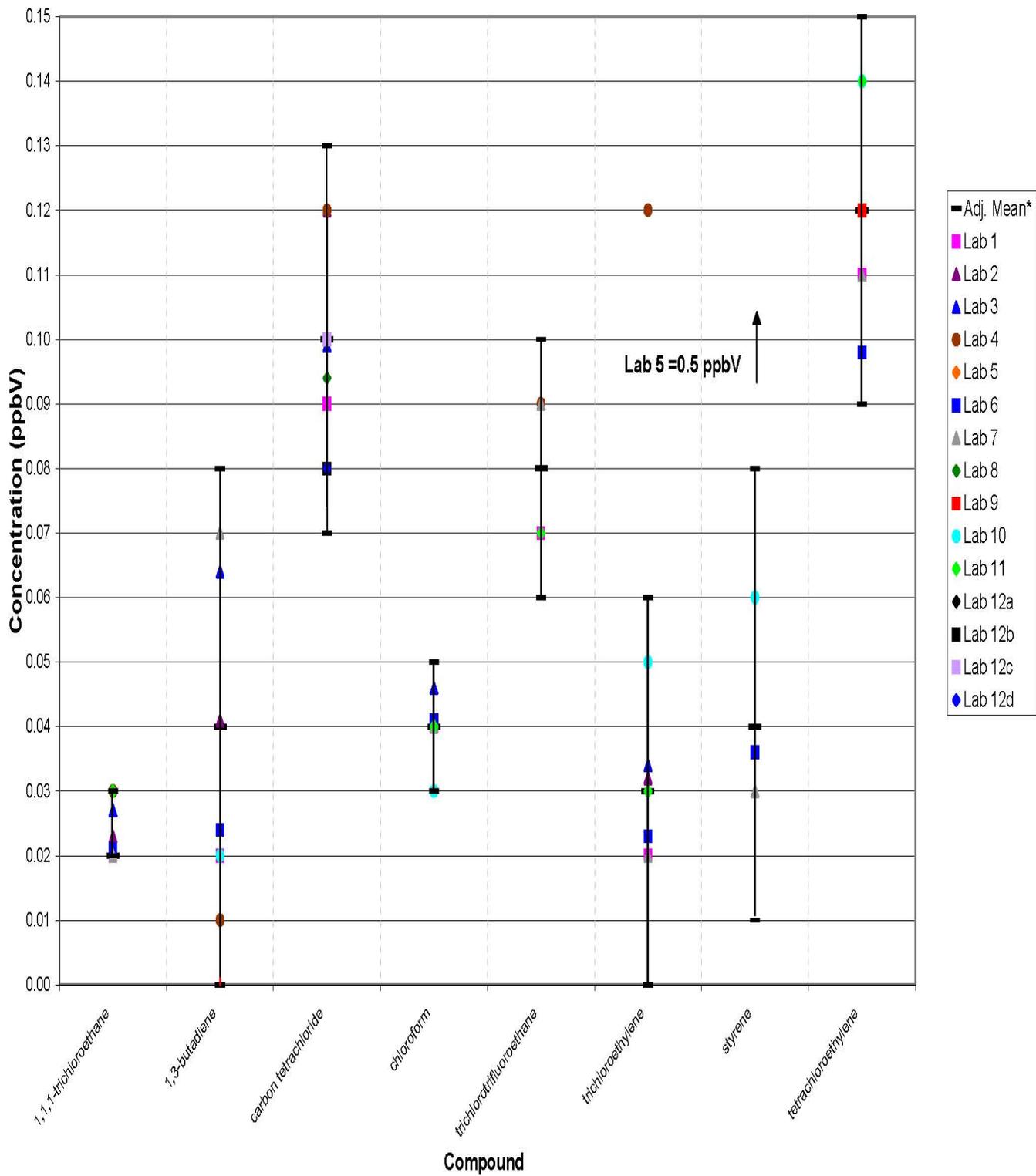
The audit programs contained two elements in 2005: laboratory audits and a whole air comparison check. The audit results and several papers that discuss these elements of the QA program in detail are available at <http://www.arb.ca.gov/aaqm/toxics.htm>.

Accuracy (field):

In 2005, a whole air comparison check was conducted to compare the analytical methods used by all the laboratories that measure ambient concentrations of toxic compounds. The purpose of the comparison check is to verify the comparability of the analytical methods currently used by those laboratories measuring ambient concentrations of gaseous toxic compounds. A specially designed sampler draws ambient air for 3 hours, filling up to 12 canisters at a time, to an approximate pressure of 14 pounds per square inch gauge (psig) each. A canister is then sent to each participating laboratory for analysis. The laboratories follow their standard operating procedures in assaying the contents and report their results to QAS for comparison. As can be seen below in Figure C1, the twelve participating laboratories compared well for most compounds. If any laboratory's response for a compound was not consistent with the other laboratory's responses, it was notified of the discrepancy.

Figure C1. (Continued on next page)

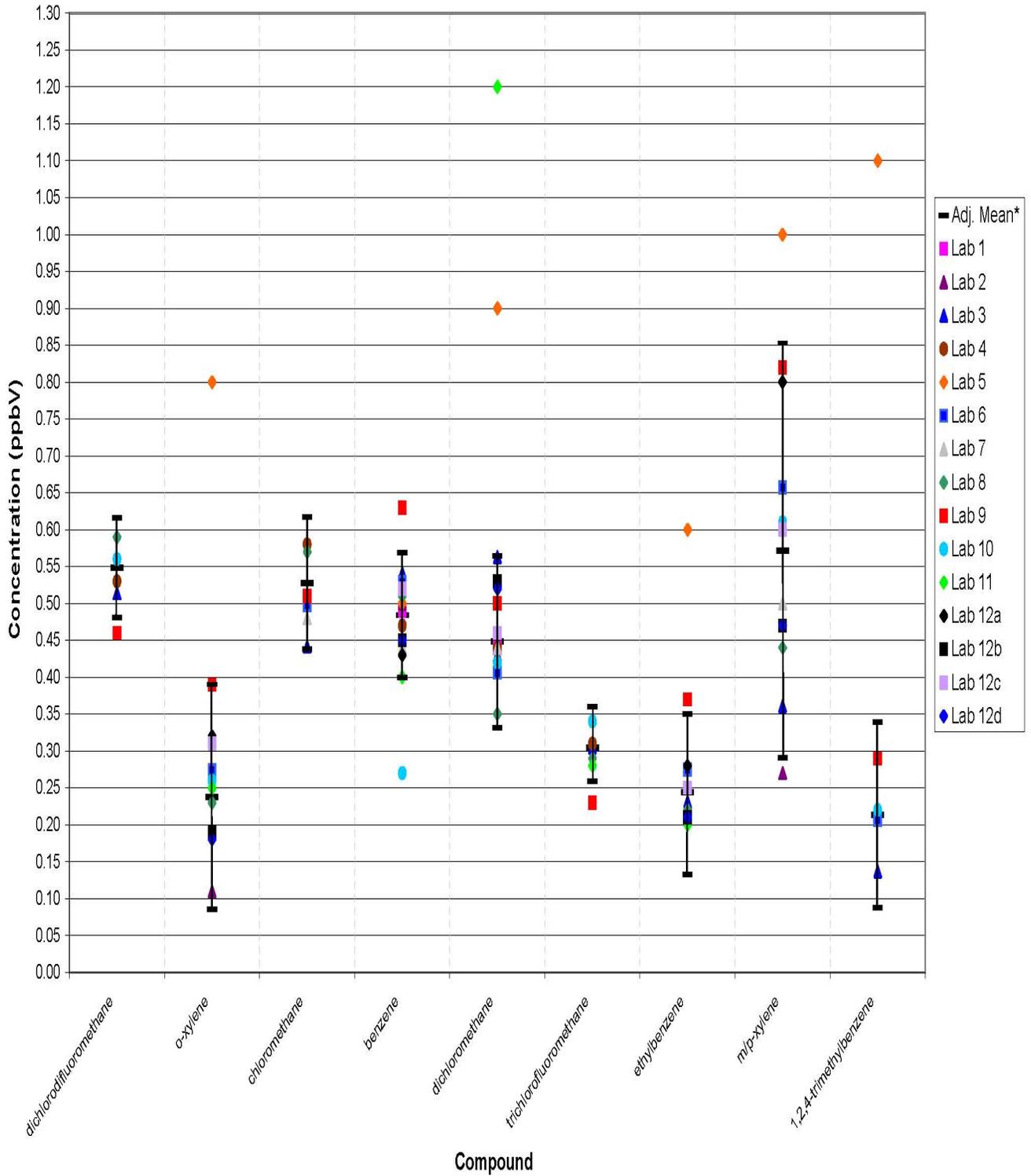
2005 Ambient Air Toxics Laboratory Comparison Check



* Plot of the adjusted mean includes +/-2 standard deviation error bars.

Figure C1. (continued on next page)

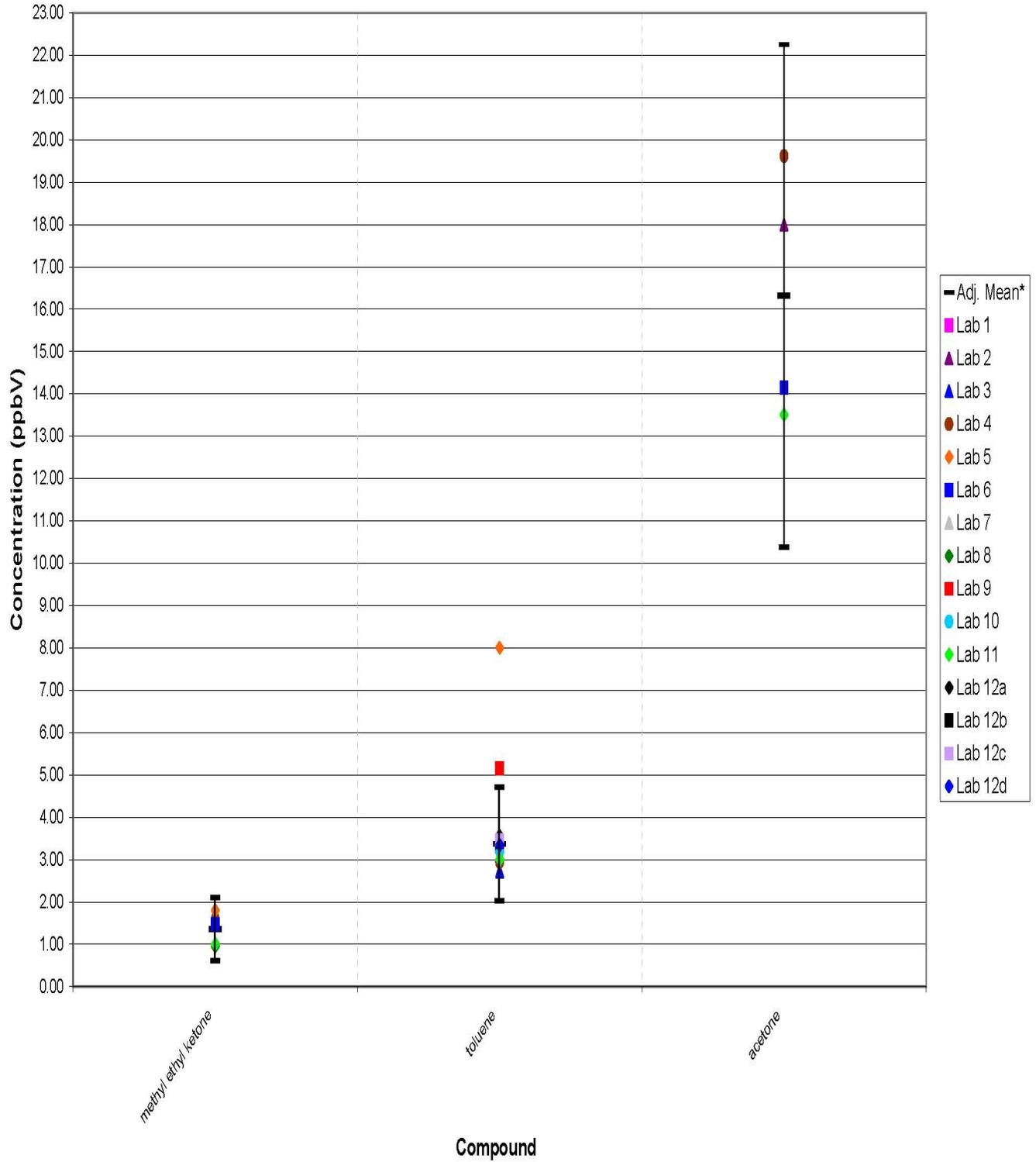
2005 Ambient Air Toxics Laboratory Comparison Check (cont.)



* Plot of the adjusted mean includes +/-2 standard deviation error bars.

Figure C1. (continued from previous pages)

2005 Ambient Air Toxics Laboratory Comparison Check (cont.)



* Plot of the adjusted mean includes +/-2 standard deviation error bars.

Flow audits of the toxic metal and carbonyl sampler (shown right) are typically conducted annually at each site to ensure the accuracy of measuring toxic metals and carbonyl compounds. Flow rates are a determining factor in calculating concentration and are included as part of the quality assurance program.



Toxic Metals and Carbonyl Sampler

Overall, the 2005 results indicate that the samplers maintained stable flows. Ninety-eight percent of the instruments audited operated within the ARB’s control limits of +/-15%. Although toxics data are a descriptive data set, AQDAs are issued based on the operating parameters of the sampler. Corrections are made to the data if an audit is found to be outside the ARB’s control limits. Instruments operating outside of ARB’s control limits resulted in zero days of invalidated flow rate data.

Table C1 shows the differences from the certified value of the individual audit points for each pollutant. The upper and lower probability limits represent the expected accuracy of 95 percent of all the single analyzer’s individual percent differences for all audit test levels at a single site. Audit results were not used in the statistical analysis shown below if the ambient data was invalidated due to an AQDA.

Table C1. 2005 Results for Toxic Air Sampler Flow Rate Performance Audits Conducted by ARB

| Pollutant | Number of Samplers Audited | Number of AQDAs | Average % Difference | Probability Limits | |
|--------------|----------------------------|-----------------|----------------------|--------------------|-------|
| | | | | 95%UL | 95%LL |
| Cr6+ | 30 | 0 | -0.4 | 6.5 | -7.3 |
| Total Metals | 32 | 0 | 0.3 | 9.0 | -8.4 |
| Aldehydes | 29 | 1 | 0.7 | 9.4 | -8.0 |

Source: Quality Assurance Section, *Accuracy Estimates*

Accuracy (lab): Laboratory performance audits are conducted annually to determine the accuracy of a laboratory to measure ambient VOC concentrations. Summary statistics of ARB’s audit results are shown in Table C2. The percent difference presented in the table represents the average difference between the laboratory’s measured value and the NIST certified value. The audit results for 2005 showed that nearly all of the compounds were within ±20 percent of the NIST certified values; except for carbon tetrachloride and trans-1,3-dichloropropene.

Table C2. ARB's 2005 Toxic Air Contaminants Laboratory Performance Audit Results

| Compound | ARB Laboratory |
|-------------------------|----------------|
| | % Diff |
| Benzene | -0.6 |
| Bromomethane | -0.3 |
| 1,3-Butadiene | -13.2 |
| Carbon Tetrachloride | -33.5 |
| Chloroform | -4.0 |
| ortho-Dichlorobenzene | -7.6 |
| para-Dichlorobenzene | -8.6 |
| Ethylbenzene | -6.5 |
| Methyl Chloroform | -7.2 |
| Methylene Chloride | -3.6 |
| Perchloroethylene | -1.7 |
| Styrene | -8.6 |
| Toluene | -5.7 |
| Trichloroethylene | -1.7 |
| m/p-Xylene | -1.6 |
| o-Xylene | -5.2 |
| cis-1,3-Dichloropropane | -19.6 |
| 1,3-Dichloropropane | -34.9 |

Precision (field and lab): As part of the TAC Program laboratory analyses, internal QC techniques such as blanks, control samples, and duplicate samples are applied to ensure the precision of the analytical methods and that the toxics data are within statistical control. Precision data for non-continuous toxics particulate samplers are obtained through collocated sampling whereby two identical samplers operate side-by-side simultaneously and the same laboratory conducts filter analyses. Collocated toxic samplers are located at selected sites and are intended to represent overall network precision.

In 2005, all compounds analyzed were within their respective control limits and results for blanks, spikes, and duplicate samples established in the Laboratory QC Manual. Duplicate analyses were performed on 10% of the toxic samples. In 2005, all duplicate results with concentrations greater than five times the published LODs were within the established limits for all target analytes. Data exceeding duplicate criteria of three times the assigned percent relative standard deviation (from control samples collected during the control limit evaluation) are deleted from the toxics database and samples reanalyzed.

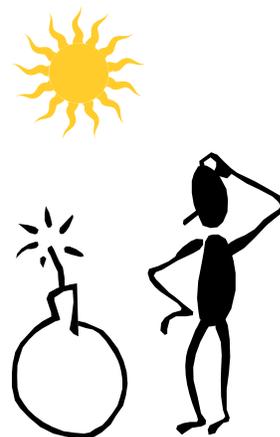
Stainless steel canisters used to collect ambient air samples are also checked for contamination. Canisters are analyzed for aromatic and halogenated hydrocarbons. One canister per batch of eight is assayed to ensure individual compound measurements fall below the limit of detection. In the event a compound exceeds canister cleanliness criteria, the canister and all other canisters represented in the batch are re-cleaned until compounds meet the cleanliness criteria.

The toxics audit results, which serve to assure the validity of the toxics data, and several papers that discuss the elements of the QA program in detail are available at http://www.arb.ca.gov/aaqm/qmosqual/perfaudit/toxics/qa_toxic.htm.

D. Non-Methane Hydrocarbons

PHOTOCHEMICAL ASSESSMENT MONITORING STATIONS

In 1989, ARB began a routine seasonal sampling program to gather information about non-methane hydrocarbon (NMHC) species that were precursors to ozone formation in high ozone areas. In 1994, Federal regulations required states to establish photochemical assessment monitoring stations (PAMS) as part of their State Implementation Plan monitoring networks in areas designated as serious or higher for ozone. Monitoring is to continue until the ozone standard is reached. The PAMS program is intended to supplement ozone monitoring and add detailed sampling for its precursors. PAMS sites collect data on ozone, oxides of nitrogen, real-time total NMHC, speciated hydrocarbons, carbonyls, and various ground level and aloft meteorological parameters. As this is a descriptive data set, there are currently no mandatory data quality objectives or regulations for the data. However, efforts are made to ensure that accurate data are collected and that the analyzers are operating within ARB's audit standards. Due to limited resources, the Organic Laboratory Section's involvement in the PAMS program was suspended indefinitely.



Two types of ongoing hydrocarbon performance audits are conducted (laboratory and TTP continuous analyzer) that support the canister-type collection system and the real-time analyzers. A cross-check is also run by QAS that allows all laboratories to compare their results from a *whole air sample* representing an identical parcel of air. The whole air sample element was added in 1997 and uses a system developed by QAS staff. Staff presented a paper on the program at the 2000 International Symposium on the Measurement of Toxic and Related Air Pollutants. A copy of the paper as well as other information about the PAMS quality assurance program is available at http://www.arb.ca.gov/aaqm/qmosqual/perfaudit/nmhc/qa_nmhc.htm.

Accuracy (field and lab):

Laboratory performance audits are conducted annually to assess the participating laboratory's ability to measure ambient levels of hydrocarbons. The 2005 laboratory performance audit results are shown in Table D1. The average percent difference represents the combined differences from all the laboratories audited. The 2005 audit results showed that Toluene, Octane, Orthro-Xylene, Decane and Nonane were all outside the ARB's control limits of +/-20%.

Table D1. 2005 Laboratory NMHC Audit Results for California's PAMS Network

| Compounds | Laboratory | |
|------------------------|------------|---------|
| | Avg % Diff | Std Dev |
| Ethane | -4.4 | 5.4 |
| Propane | -5.6 | 4.1 |
| Propene | -8.9 | 7.6 |
| Isobutane | -7.2 | 3.6 |
| Isobutene | -8.2 | 7.4 |
| Butane | -2.9 | 6.6 |
| 2- Methylbutane | 7.4 | 8.7 |
| Pentane | -2.2 | 12.6 |
| 1-Pentene | -15.9 | 9.6 |
| Hexane | -8.6 | 7.5 |
| Benzene | -3.5 | 9.1 |
| 2,2,4-Trimethylpentane | 4.7 | 6.2 |
| Toluene | -28.7 | 27.8 |
| Octane | -21.4 | 21.5 |
| Orthro-Xylene | -24.3 | 22.7 |
| Decane | -24.9 | 27.3 |
| Heptane | -1.8 | 10.9 |
| Nonane | -30.4 | 33.6 |

TTP continuous NMHC analyzer performance audits include audits of total NMHC analyzers (i.e., TECO 55). The 2005 TTP continuous analyzer NMHC PAMS audit results are shown in Table D2. The purpose of this table is to estimate the accuracy of the hydrocarbon data in the database. The upper and lower probability limits represent the expected accuracy of 95 percent of all the analyzer's individual percent differences for all audit test levels at a single site. Based on the audit results, ninety-four percent of the instruments audited were found to be operating within ARB's control limits of +/-15%. Audit results were not used in the statistical analysis (Table D2) if the audit was invalidated due to an AQDA that resulted in data invalidation. Out of control events are typically due to instruments that were inoperable at time of the audit, contamination of the analyzers clean air source, or inconsistent span check readings. The single AQDA issued for continuous NMHC resulted in 21 days of lost data.

Table D2. 2005 Results for TTP Continuous Analyzer NMHC PAMS Audits

| Pollutant | Number of Analyzers Audited | Number of AQDAs | Average % Difference | Probability Limits | |
|-----------|-----------------------------|-----------------|----------------------|--------------------|-------|
| | | | | 95%UL | 95%LL |
| NMHC | 16 | 1 | 1.6 | 11.8 | -8.6 |

Source: Quality Assurance Section, Accuracy Estimates

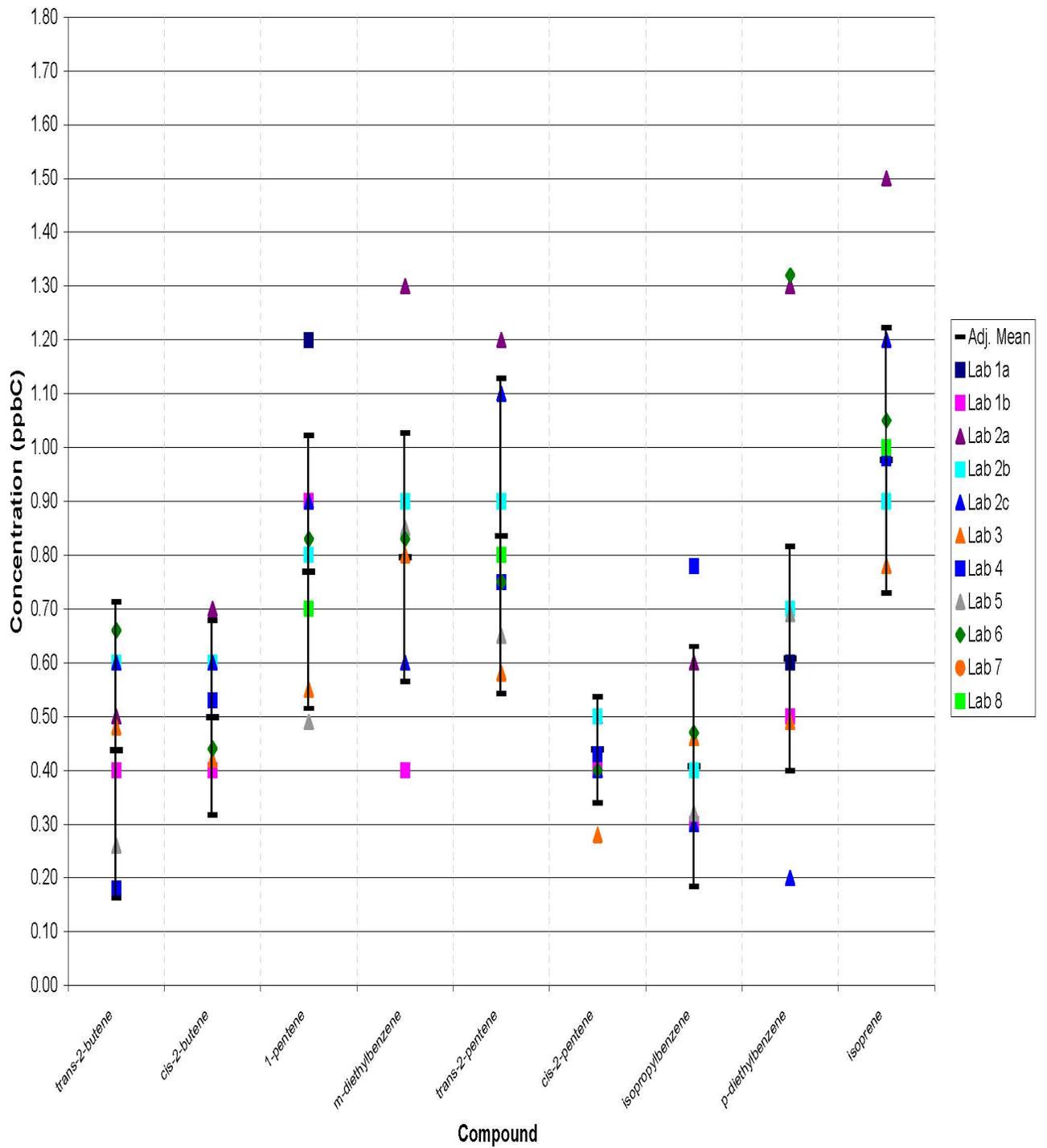
The *Whole Air Sampler* performance checks are a valuable complement to the TTP and laboratory audits. Specifically, they are a means of assessing performance using a sample that includes non-target species and other aspects of a real world sample that could potentially affect sample results. It involves all California PAMS laboratories that measure ambient concentrations of hydrocarbons as well as others choosing to participate. The performance check uses a specially designed sampler that draws ambient air for 3 hours simultaneously into 12 canisters at a time. Each canister reaches approximately 14 pounds per square inch gauge (psig) of pressure. This replicates a normal sample duration and pressure. A canister is sent to each participating laboratory for speciated NMHC analysis. The laboratories follow their standard operating procedures in assaying the contents and report their results to QAS.

The 2005 Whole Air Comparison Check results are shown in Figure D3. Based on the results, the laboratory responses compared well for most compounds. If any laboratory's response for a compound was not consistent with all other participating laboratory responses, the laboratory was notified of the discrepancy. The whole air comparison check results are available at

<http://www.arb.ca.gov/aaqm/qmosqual/perfaudit/nmhc/whole/wholetable.htm>

Figure D3. (Continued on next page)

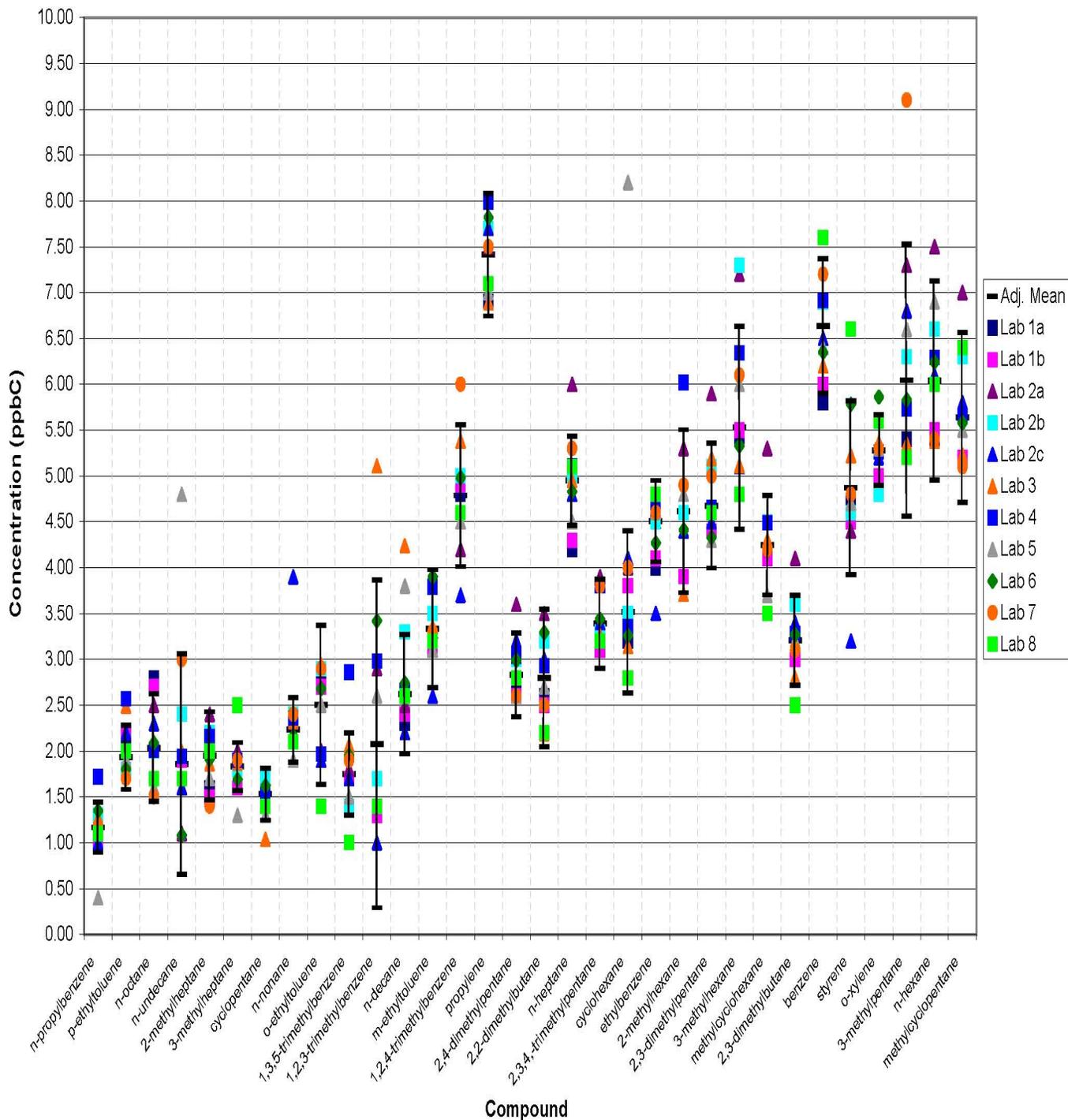
2005 Ambient Air Non-Methane Hydrocarbon Laboratory Comparison Check



* Plot of the adjusted mean includes ± 2 standard deviation error bars.

Figure D3. (Continued on next page)

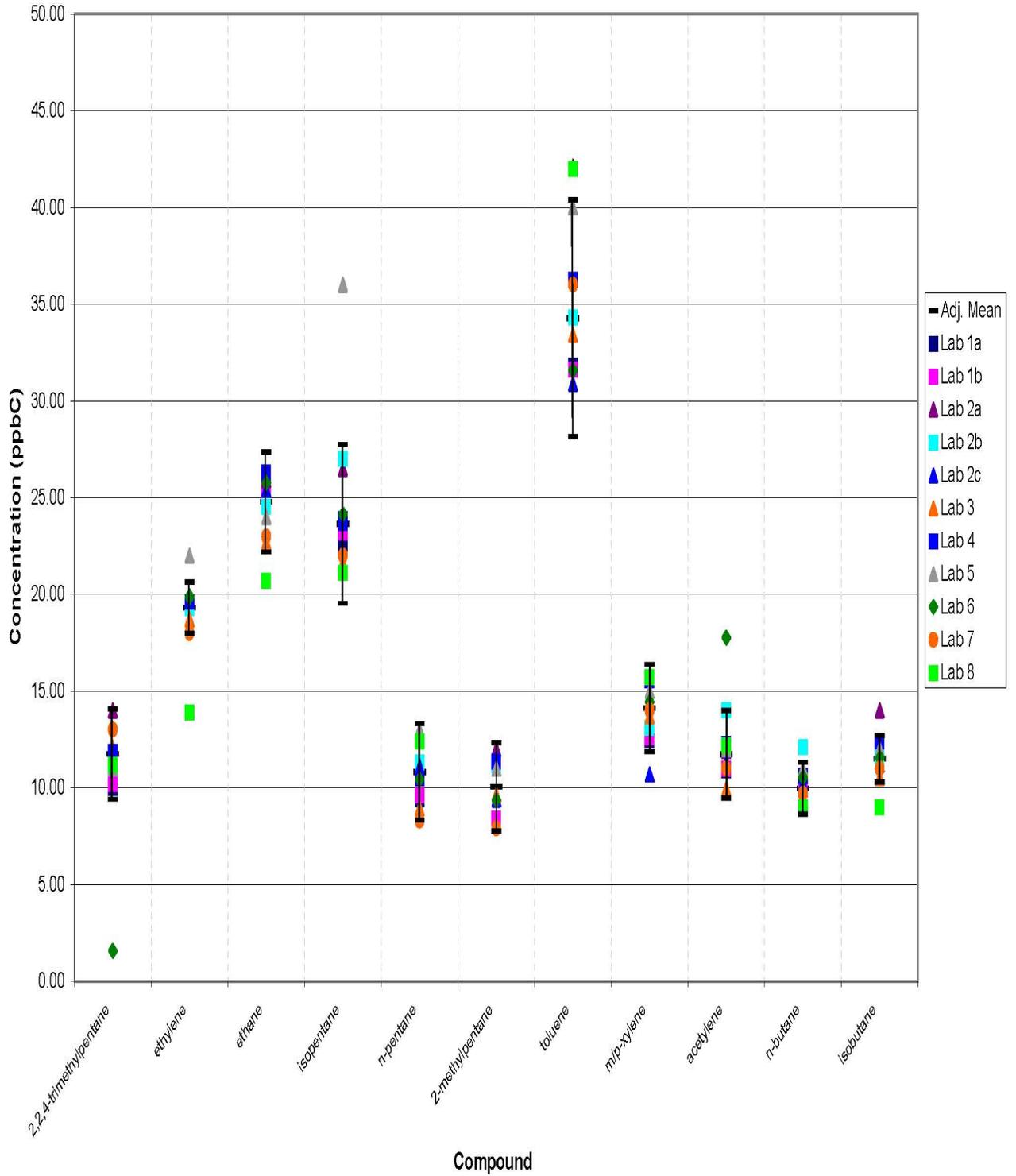
2005 Ambient Air Non-Methane Hydrocarbon Laboratory Comparison Check (cont.)



* Plot of the adjusted mean includes +/- standard deviation error bars.

Figure D3. (Continued on next page)

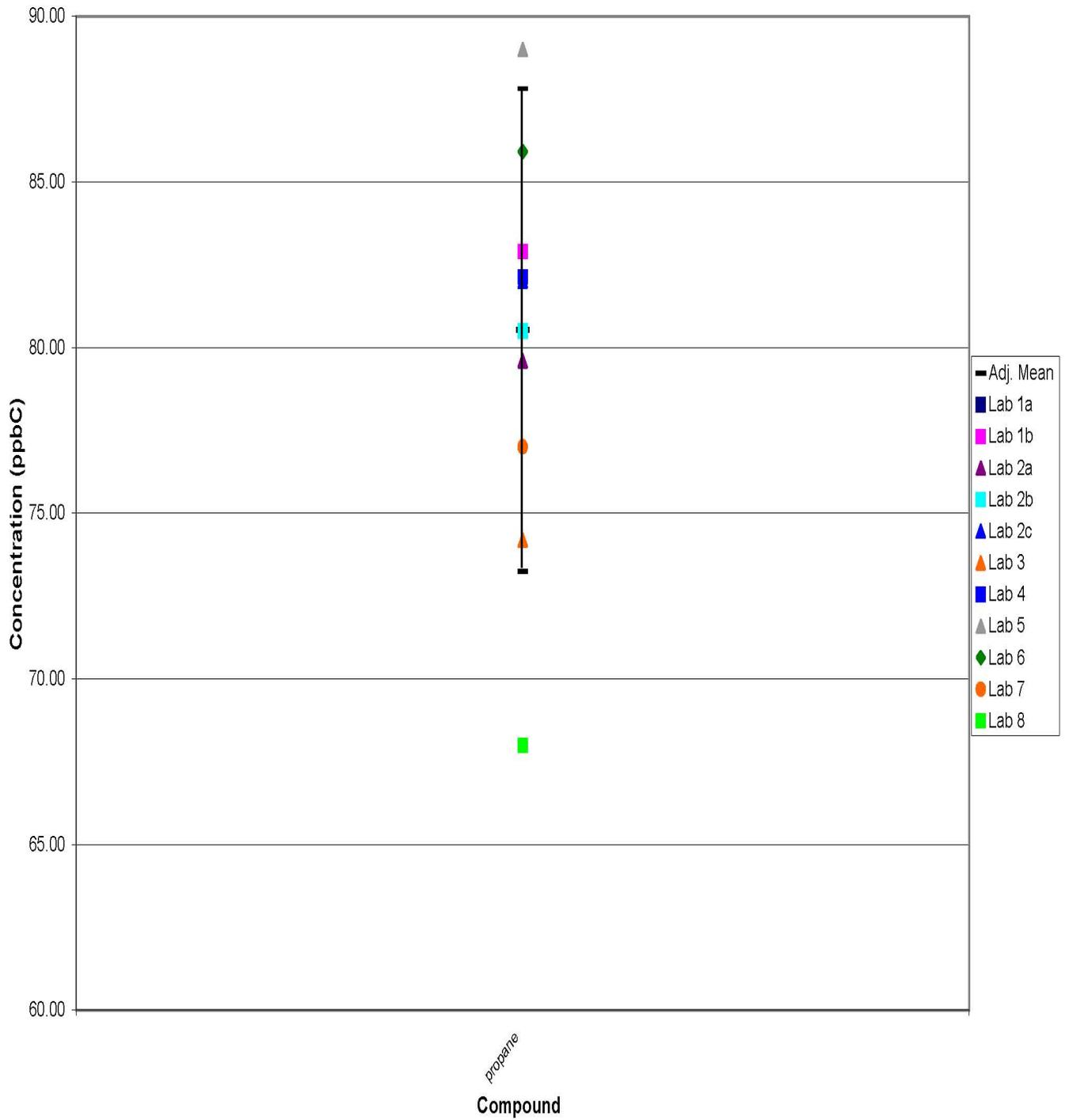
2005 Ambient Air Non-Methane Hydrocarbon Laboratory Comparison Check (cont.)



* Plot of the adjusted mean includes ± 2 standard deviation error bars.

Figure D3. (Continued from previous pages)

2005 Ambient Air Non-Methane Hydrocarbon Laboratory Comparison Check (cont.)



* Plot of the adjusted mean includes +/-2 standard deviation error bars.

MOTOR VEHICLE EXHAUST PROGRAM

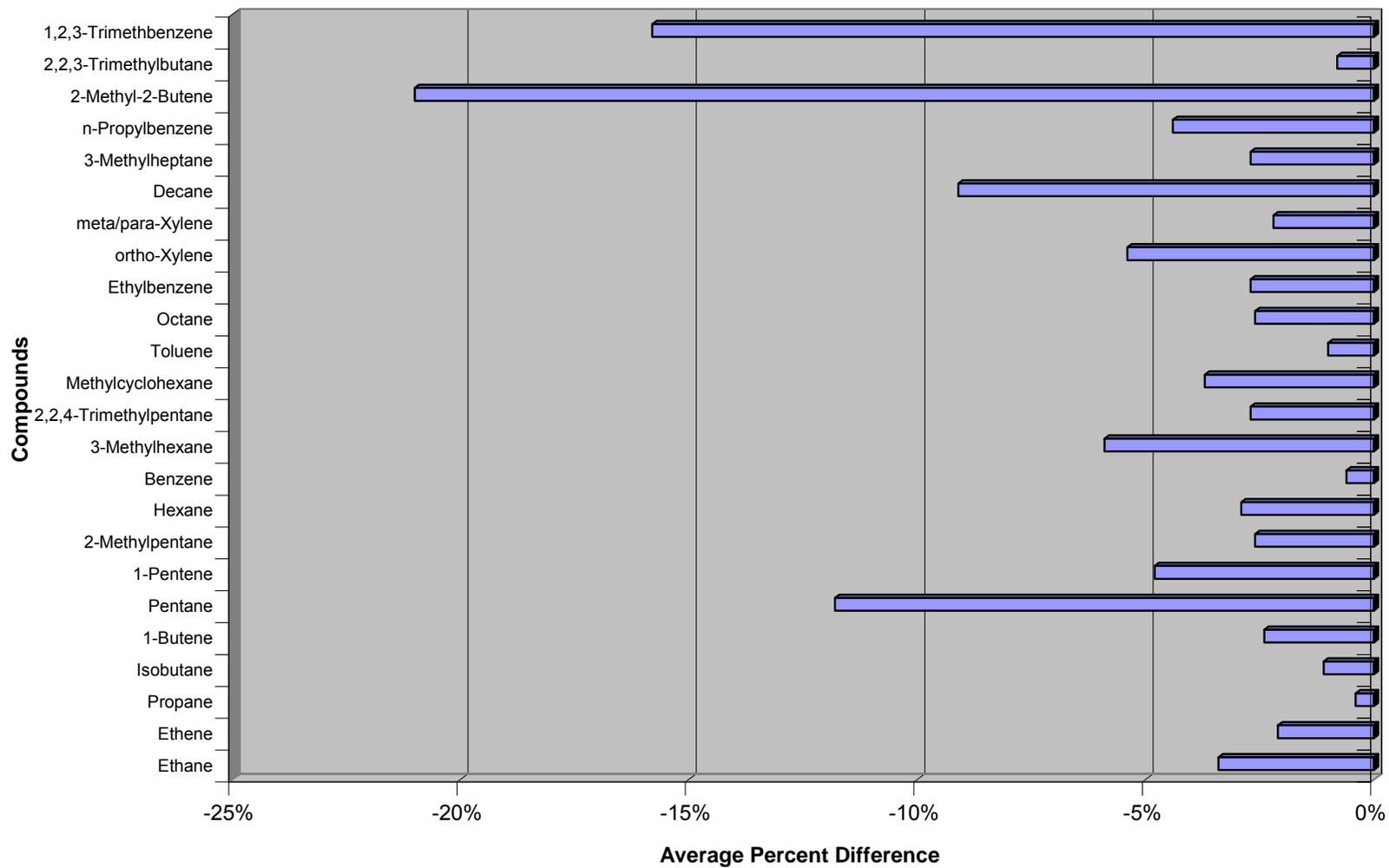
The QAS motor vehicle exhaust audit program supports ARB's efforts in determining the reactivity of fuel components found in automotive exhaust samples. The exhaust and fuels information can be compared to the regulatory standard for non-methane organic gases tail-pipe emissions, fuel composition, and a number of ozone precursors. Special studies are currently being conducted to determine emissions generated from vehicles operated under manufacturers recommendations.



Emissions Sampling

Accuracy: Laboratory performance audits are conducted annually of the Southern Laboratory Branch of ARB for components of motor vehicle exhaust collected while a vehicle was operated on a dynamometer. The laboratory results for 2005 are shown in Figure D4. Overall, the performance audit results showed that all of the compounds were within ARB's control limits of $\pm 20\%$ except for 2-Methyl-2-Butene.

Figure D4. Motor Vehicle Exhaust Audit Results for Southern Laboratory Branch



E. Dioxin



Dioxin Sampler

Dioxins and furans are highly toxic chemicals that are formed as unwanted by-products during the combustion of materials and the manufacturing of certain chlorinated chemicals. Dioxins and furans are emitted into the atmosphere from a variety of sources including vehicles, waste incinerators, chemical manufacturing plants, and other industrial sources that burn fuel. Dioxins are highly persistent and can accumulate in the lungs and abdominal cavity for long periods of time. Studies have shown that exposure to dioxins can cause cancer and other health problems including birth defects and liver damage. Infants and children are especially susceptible to illness from dioxin exposure, which can cause immune and developmental system toxicity.

The ARB established the California Ambient Dioxin Air Monitoring Program (CADAMP) to provide information on ambient levels of dioxins and dioxin-like compounds (furans, polychlorinated biphenyls and polybrominated diphenyl ethers) in populated urban areas.

On December 20, 2001, the ARB began conducting ambient air monitoring for dioxins, furans and dioxin-like polychlorinated biphenyls (PCBs) at CADAMP sites. From December 2001 through December 2004, ten sampling sites made up the CADAMP network, five in the San Francisco Bay area, an additional site in Sacramento, and four in the Los Angeles basin. Several of the dioxin monitors operated in parallel with air monitoring stations in ARB's Children's Environmental Health Protection Program network.

The CADAMP monitoring schedule initially consisted of thirteen sampling periods in which samplers are operated continuously for six days followed by one day of inactivity, totaling twenty-four days of sample (or 576 hours of sample) per sampling period. In January 2004, sampling was reduced to five days followed by two days of inactivity.

In 2005, all of the original sites were decommissioned except for one in the Bay Area and one in the South Coast. The purpose of the 2005 sampling effort was to continue very limited CADAMP monitoring in the two largest urban areas of the State while a one-year extension of the program was initiated in the San Joaquin Valley. The program extension included adding two sites in Fresno County: one in the city of Fresno and the other in Five Points. Monitoring at Five Points is representative of a non-industrial, low population, rural area in Fresno County. This will allow for comparisons to the high-population, industrialized, urban CADAMP sites.

Ambient air samples are analyzed by a contract laboratory for dioxins/furans, PCBs, and polybrominated diphenyl ethers (PBDEs). Information about CADAMP is available at <http://www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm>. Information about the ambient air monitoring that supports measuring children's exposure to air pollution in our communities is at <http://www.arb.ca.gov/ch/ch.htm>.

F. Asbestos

Asbestos is a term used for several types of asbestiform fibers that include naturally occurring fibrous varieties of the minerals serpentine and amphibole. Naturally Occurring Asbestos (NOA) is commonly associated with ultramafic and serpentine rocks which can be found in many parts of California. Asbestos is released when these rocks are broken or crushed. Once released from the rocks, asbestos can become airborne and may remain in the environment for long periods of time.



Asbestos samplers

Asbestos is a known carcinogen. Inhalation of asbestos may result in the development of lung cancer or mesothelioma. Emissions sources include unpaved roads or driveways covered with ultramafic or serpentine rock aggregate, and construction or rocks quarrying activities in areas containing ultramafic and serpentine rocks. Other sources of asbestos are in man-made products. These are also released naturally through weathering and erosion.

In 1986, ARB identified naturally-occurring asbestos as a toxic air contaminant (TAC) and subsequently adopted two Airborne Toxic Control Measures (ATCM) to address some of the health concerns associated with asbestos exposure caused by these activities. The measures prohibit the use of serpentine or ultramafic rocks containing $\geq 0.25\%$ asbestos for unpaved surfacing materials and controls dust emissions from construction, grading, and surface mining in areas where ultramafic and serpentine rocks are present.

Information about naturally occurring asbestos is available at <http://www.arb.ca.gov/toxics/asbestos/asbestos.htm>

G. Consumer Products



Consumer products are chemically formulated products used by the public in homes and businesses. These compounds are reported to emit approximately 260 tons per day of smog-forming VOCs. Monitoring VOC levels in consumer products and finding ways to reduce VOC emissions they contain facilitates ARB's effort to reduce smog in the State.

Consumer products are descriptive data sets. Informal data quality objectives have been established and staff ensures the accuracy and precision for data quality are met. Information about the Consumer Products Program is available at <http://www.arb.ca.gov/consprod/consprod.htm>.

Accuracy (lab): The QAS does not conduct performance audits on the Consumer Product Program at this time. The Special Analysis Section of the Northern Laboratory Branch performs internal quality control activities such as limits of detection, duplicates/replicates, calibrations, control and check samples, blanks, and trip standards to verify statistical control among analytical methods and ensure valid data are generated.

Precision (lab): Analytical precision is derived from duplicate analysis performed on a minimum of 10% of the samples. The results from the analyses are compared, and the difference should be less than $\pm 3\%$. A sample outside the acceptance criteria prompts staff to investigate quality control activities to verify data generated are valid. However, since the acceptance criteria of the method is only $\pm 3\%$, the data is not necessarily invalidated when the sample is in a difficult matrix and has a low percentage of volatile organic compounds. Following an investigation of the problem, samples are re-analyzed when required. Table G1 shows the duplicate data for the 1st quarter of 2005. Further data are available upon request.

Table G1. Duplicate Final %VOC Results for 1st Quarter 2005.

| n= 61 | | Absolute % Difference | Relative % Difference |
|--------------|--------------|-----------------------|-----------------------|
| Duplicate #1 | Duplicate #2 | | |
| % VOC | | | |
| 56.82 | 55.28 | 1.55 | 2.76 |
| 0.24 | 0.50 | 0.25 | 69.26 |
| 8.65 | 8.01 | 0.63 | 7.59 |
| 3.30 | 3.49 | 0.18 | 5.39 |
| 1.56 | 1.31 | 0.25 | 17.19 |
| 12.50 | 12.44 | 0.06 | 0.50 |
| 63.49 | 63.56 | 0.08 | 0.12 |
| 43.87 | 43.38 | 0.49 | 1.11 |
| 5.62 | 5.13 | 0.49 | 9.13 |
| <0.1 | <0.1 | 0.00 | 0.00 |
| 1.46 | 0.17 | 1.29 | 157.25 |
| 56.57 | 56.86 | 0.29 | 0.51 |
| 54.78 | 54.67 | 0.11 | 0.20 |
| 23.21 | 23.67 | 0.45 | 1.94 |
| 6.49 | 6.58 | 0.10 | 1.49 |
| 21.27 | 21.27 | 0.00 | 0.00 |
| 13.01 | 12.67 | 0.33 | 2.60 |
| 54.05 | 54.08 | 0.03 | 0.06 |
| 6.25 | 6.34 | 0.09 | 1.40 |
| 81.03 | 81.16 | 0.12 | 0.15 |
| 21.29 | 21.25 | 0.05 | 0.21 |
| 22.26 | 22.40 | 0.14 | 0.62 |
| 5.57 | 3.65 | 1.92 | 41.63 |
| 3.25 | 3.42 | 0.17 | 5.18 |
| 55.10 | 55.12 | 0.02 | 0.04 |
| 53.87 | 53.75 | 0.12 | 0.23 |
| 9.18 | 8.03 | 1.15 | 13.42 |
| 52.87 | 52.62 | 0.26 | 0.49 |
| 3.60 | 2.59 | 1.01 | 32.72 |
| 47.98 | 46.73 | 1.26 | 2.65 |
| 53.52 | 53.79 | 0.27 | 0.51 |
| 10.61 | 10.02 | 0.60 | 5.79 |
| 11.76 | 12.11 | 0.35 | 2.95 |
| 34.46 | 35.13 | 0.67 | 1.91 |
| 5.02 | 5.11 | 0.09 | 1.80 |
| 77.01 | 77.32 | 0.31 | 0.41 |
| 61.17 | 61.27 | 0.10 | 0.17 |
| 12.55 | 12.71 | 0.16 | 1.25 |
| 55.40 | 55.18 | 0.23 | 0.41 |
| 3.37 | 1.38 | 1.99 | 83.71 |
| 55.44 | 55.44 | 0.00 | 0.01 |
| 75.74 | 75.80 | 0.06 | 0.07 |
| <0.1 | <0.1 | 0.00 | 0.00 |
| 97.00 | 97.00 | 0.00 | 0.00 |
| 1.98 | 2.04 | 0.07 | 3.29 |
| 53.38 | 53.30 | 0.08 | 0.15 |
| 10.16 | 11.54 | 1.39 | 12.77 |
| 25.89 | 25.93 | 0.04 | 0.14 |
| 3.38 | 4.97 | 1.59 | 37.97 |
| 15.96 | 14.81 | 1.14 | 7.43 |
| 10.81 | 10.87 | 0.06 | 0.58 |
| 6.77 | 7.21 | 0.45 | 6.41 |
| 19.17 | 19.28 | 0.11 | 0.58 |
| 8.07 | 9.23 | 1.15 | 13.35 |
| 2.36 | 3.86 | 1.51 | 48.54 |
| 5.61 | 5.26 | 0.35 | 6.45 |
| 61.22 | 61.72 | 0.50 | 0.82 |
| 52.57 | 53.00 | 0.43 | 0.81 |
| 47.90 | 49.87 | 1.97 | 4.03 |
| 73.19 | 73.18 | 0.00 | 0.01 |
| 98.37 | 98.47 | 0.10 | 0.10 |
| 8.72 | 8.55 | 0.17 | 1.97 |
| 54.55 | 54.15 | 0.39 | 0.72 |

Note: Diff = ABS (Dup 1 – Dup 2)

The Special Analysis Section laboratory analyzes known standards (trip standards) to establish control limits and limits of detection, runs system blanks to confirm the system is not contaminated, and conducts yearly multi-point calibrations to assess the instrument linearity.

Presently, trip standards should meet the established acceptance criteria of +/-3% difference. A sample outside the acceptance criteria prompts staff to investigate quality control activities to verify data generated are valid. However, since the acceptance criteria of the method is only $\pm 3\%$, the data is not necessarily invalidated when the sample is in a difficult matrix and has low percentage of volatile organic compounds. Overall, the analytical precision results indicate that the laboratory is providing precise consumer product data. Table G2 represents the trip standard results for the 1st quarter of 2005. Further data are available upon request.

Table G2. Trip Standard Results for 1st Quarter 2005.

| n= 62 | | | | | | |
|---------------------------------|---------------|---------------|-----------------|-----------------|------------------|------------------|
| Total Volatile Material (SAS01) | Water (SAS03) | Water (SAS04) | Acetone (SAS07) | Ethanol (SAS07) | Methanol (SAS07) | Calculated % VOC |
| weight fraction | | | | | | |
| 0.90 | 0.58 | 0.63 | 0.10 | 0.10 | 0.10 | 19.76 |
| 0.90 | 0.59 | 0.60 | 0.09 | 0.09 | 0.09 | 21.13 |
| 0.90 | 0.57 | 0.59 | 0.10 | 0.10 | 0.10 | 21.58 |
| 0.90 | 0.58 | 0.60 | 0.10 | 0.09 | 0.10 | 21.31 |
| 0.90 | 0.58 | 0.62 | 0.10 | 0.10 | 0.10 | 19.97 |
| 0.90 | 0.57 | 0.60 | 0.09 | 0.09 | 0.09 | 22.71 |
| 0.90 | 0.60 | 0.62 | 0.10 | 0.10 | 0.10 | 18.75 |
| 0.90 | 0.62 | 0.62 | 0.09 | 0.10 | 0.10 | 18.69 |
| 0.90 | 0.61 | 0.61 | 0.10 | 0.10 | 0.10 | 19.28 |
| 0.90 | 0.61 | 0.62 | 0.10 | 0.10 | 0.10 | 18.61 |
| 0.90 | 0.61 | 0.61 | 0.11 | 0.10 | 0.11 | 18.24 |
| 0.90 | 0.58 | 0.64 | 0.09 | 0.09 | 0.94 | 19.63 |
| 0.90 | 0.59 | 0.60 | 0.09 | 0.09 | 0.09 | 21.17 |
| 0.90 | 0.60 | 0.60 | 0.09 | 0.09 | 0.09 | 20.65 |
| 0.90 | 0.61 | 0.62 | 0.10 | 0.10 | 0.10 | 18.45 |
| 0.90 | 0.60 | 0.61 | 0.10 | 0.10 | 0.10 | 19.83 |
| 0.90 | 0.61 | 0.62 | 0.09 | 0.10 | 0.10 | 18.99 |
| 0.90 | 0.60 | 0.61 | 0.10 | 0.10 | 0.10 | 19.76 |
| 0.90 | 0.59 | 0.61 | 0.09 | 0.09 | 0.09 | 20.91 |
| 0.90 | 0.62 | 0.60 | 0.09 | 0.09 | 0.09 | 20.12 |
| 0.90 | 0.60 | 0.61 | 0.09 | 0.09 | 0.09 | 20.28 |
| 0.90 | 0.61 | 0.60 | 0.10 | 0.10 | 0.10 | 19.53 |
| 0.90 | 0.59 | 0.63 | 0.10 | 0.10 | 0.10 | 18.90 |
| 0.90 | 0.58 | 0.62 | 0.09 | 0.09 | 0.09 | 20.64 |
| 0.90 | 0.58 | 0.61 | 0.09 | 0.10 | 0.10 | 21.40 |
| 0.90 | 0.61 | 0.60 | 0.10 | 0.10 | 0.10 | 19.93 |
| 0.90 | 0.60 | 0.61 | 0.09 | 0.09 | 0.09 | 20.43 |
| 0.90 | 0.58 | 0.59 | 0.09 | 0.09 | 0.10 | 22.24 |
| 0.90 | 0.59 | 0.61 | 0.09 | 0.09 | 0.09 | 20.72 |
| 0.90 | 0.59 | 0.60 | 0.09 | 0.09 | 0.09 | 21.13 |
| 0.90 | 0.60 | 0.59 | 0.10 | 0.10 | 0.10 | 20.48 |
| 0.90 | 0.58 | 0.63 | 0.09 | 0.10 | 0.10 | 20.09 |
| 0.90 | 0.58 | 0.59 | 0.10 | 0.10 | 0.10 | 21.06 |
| 0.90 | 0.59 | 0.60 | 0.10 | 0.09 | 0.11 | 20.11 |
| 0.90 | 0.58 | 0.62 | 0.10 | 0.09 | 0.11 | 19.69 |
| 0.90 | 0.59 | 0.63 | 0.09 | 0.08 | 0.10 | 20.30 |
| 0.90 | 0.59 | 0.61 | 0.10 | 0.09 | 0.10 | 20.25 |
| 0.90 | 0.59 | 0.61 | 0.10 | 0.09 | 0.10 | 20.33 |
| 0.90 | 0.57 | 0.60 | 0.10 | 0.09 | 0.10 | 21.85 |
| 0.90 | 0.60 | 0.61 | 0.11 | 0.10 | 0.11 | 18.62 |
| 0.90 | 0.60 | 0.60 | 0.10 | 0.09 | 0.10 | 20.07 |
| 0.90 | 0.59 | 0.60 | 0.10 | 0.09 | 0.11 | 20.27 |
| 0.90 | 0.60 | 0.60 | 0.10 | 0.09 | 0.11 | 19.80 |
| 0.90 | 0.56 | 0.59 | 0.10 | 0.09 | 0.10 | 22.58 |
| 0.90 | 0.60 | 0.60 | 0.10 | 0.09 | 0.11 | 20.03 |
| 0.90 | 0.58 | 0.60 | 0.10 | 0.10 | 0.11 | 20.76 |
| 0.90 | 0.58 | 0.63 | 0.09 | 0.10 | 0.10 | 20.01 |
| 0.90 | 0.58 | 0.62 | 0.10 | 0.09 | 0.10 | 19.98 |
| 0.90 | 0.58 | 0.61 | 0.10 | 0.09 | 0.11 | 19.92 |
| 0.90 | 0.60 | 0.60 | 0.10 | 0.09 | 0.11 | 19.71 |
| 0.90 | 0.59 | 0.60 | 0.10 | 0.09 | 0.10 | 20.59 |
| 0.90 | 0.62 | 0.60 | 0.10 | 0.09 | 0.11 | 19.22 |
| 0.90 | 0.59 | 0.59 | 0.09 | 0.09 | 0.10 | 21.37 |
| 0.90 | 0.60 | 0.62 | 0.09 | 0.08 | 0.10 | 19.94 |
| 0.90 | 0.61 | 0.62 | 0.10 | 0.09 | 0.10 | 18.54 |
| 0.90 | 0.59 | 0.62 | 0.10 | 0.09 | 0.11 | 19.22 |
| 0.90 | 0.59 | 0.63 | 0.10 | 0.09 | 0.10 | 19.31 |
| 0.90 | 0.59 | 0.60 | 0.09 | 0.09 | 0.10 | 21.28 |
| 0.90 | 0.59 | 0.62 | 0.10 | 0.09 | 0.11 | 19.32 |
| 0.90 | 0.59 | 0.61 | 0.09 | 0.08 | 0.09 | 21.04 |
| 0.90 | 0.58 | 0.62 | 0.10 | 0.09 | 0.10 | 20.24 |
| 0.90 | 0.57 | 0.62 | 0.10 | 0.09 | 0.10 | 20.33 |
| 0.90 | 0.60 | 0.60 | 0.10 | 0.10 | 0.10 | 20.00 |

H. Meteorology



Meteorological Tower

The ARB monitors meteorological parameters such as wind speed, wind direction, ambient temperature, relative humidity, barometric pressure, and total solar radiation. Real-time meteorological data are generated to characterize meteorological processes such as transport and diffusion, and to make air quality forecasts and burn-day decisions. The data are also used for control strategy modeling and urban airshed modeling. A State/local meteorology subcommittee of the Air Monitoring Technical Advisory Committee (AMTAC) agreed to define the level of acceptability for meteorological data as those used by the U.S. EPA for both the Prevention of Significant Deterioration (PSD) and Photochemical Assessment Monitoring Stations (PAMS) programs. The QAS audits to those levels.

The data variability collected by this element of the monitoring program are generally described as meeting or not meeting the PSD requirements. No mandatory corrections are made to the data. However, station operators are notified whether they passed the audit or not. Most operators make the effort to meet the audit standards. The wind speed, wind direction and outside temperature data sets are controlled data sets, and subject to meeting PAMS objectives. Since the inception of the meteorological audit program, the data quality have improved significantly.

Accuracy (field): The accuracy of meteorological sensors are checked by annual performance audits. Table H1 summarizes the 2005 audit results. The average difference (average degree difference with respect to ambient temperature) represents the combined differences from the certified value of all the individual audit points for each sensor. The upper and lower probability limits represent the expected accuracy of 95 percent of all the single sensor's individual percent differences for all audit test levels at a single site. Based on the audit results, over ninety-seven percent of the instruments audited were found to be operating within the ARB's control limits. The Instrument operating outside of ARB's control limits resulted in 367 days of invalidated data. Audit results were not used in statistical analysis if the audit was invalidated due to an AQDA that resulted in data invalidation. AQDAs do not apply to relative humidity, solar radiation, and vertical wind speed audit results. The high average difference and probability limits for solar radiation are due to two audits that greatly exceeded ARB's control limits, but no AQDAs were issued. Information about the meteorological monitoring program is available at <http://www.arb.ca.gov/aaqm/met.htm>.

Table H1. 2005 Results for Meteorological Sensor Performance Audits Conducted by ARB

| Sensor | Number of Sensors Audited | Number of AQDAs | Avg Diff or Avg % Diff | Probability Limits | |
|-----------------------|---------------------------|-----------------|------------------------|--------------------|-------|
| | | | | 95%UL | 95%LL |
| Ambient Temp | 93 | 3 | -0.1 | 0.3 | -0.5 |
| Relative Humidity | 25 | NA | 1.1 | 7.7 | -5.5 |
| Wind Direction | 92 | 3 | -0.1 | 4.8 | -5.0 |
| Horizontal Wind Speed | 88 | 7 | -0.1 | 3.0 | -3.2 |
| Barometric Pressure | 42 | NA | -0.6 | 2.4 | -3.6 |
| Solar Radiation | 22 | NA | -0.2 | 7.1 | -7.5 |

NA= Not applicable

Source: Quality Assurance Section, Accuracy Estimates

III. QUALITY CONTROL REPORTS

Quality Control (QC) reports are summaries of the quality control activities conducted by all MLD laboratories to support accurate and precise measurements. These activities include: blanks, duplicates, controls, spiked samples, limits of detection, calibrations, and audit results. Currently, all MLD QC reports are reviewed by the Operations Planning and Assessment Section (OPAS) to verify that good laboratory practices are followed and to identify opportunities for data quality or process improvement. The OPAS Section makes recommendations, where appropriate, to help improve the overall quality and/or effectiveness of the data. Depending on the program, QC reports are typically prepared quarterly. Table 1 lists the QC reports submitted for review in 2005.

Table 1. Quality Control Reports Submitted to OPAS Section for Review in 2005

| Submittal Frequency | Title of QC Report | Program (s) Supported |
|---------------------|---|--|
| Quarterly | Special Analysis Section, QC Report | Consumer Products and Enforcement |
| Quarterly | QC Report for the Analysis of Motor Vehicle Exhaust | Motor Vehicle Exhaust |
| Quarterly | QC Report for the Analysis of Motor Vehicle Fuel | Motor Vehicle Fuel Specification and Enforcement |
| Quarterly | NLB Inorganics Laboratory Section QC Report | Ambient Particulate Matter |
| Quarterly | QC Report for Organic Toxics Program | Ambient Toxics |

IV. STANDARDS LABORATORY



The Standards Laboratory performs technical support and certification and verification services of calibration instruments, gases, and devices. Clients include ARB divisions, air districts, and U.S. EPA Region 9 (California, Nevada, Arizona, and Hawaii). Calibrations and certifications are performed for ozone and flow rate transfer standards, certifications of compressed gas cylinders, and verifications of ozone and flow rate primary standards, to ensure that all are NIST traceable standards. A calibration establishes a correction factor to adjust or correct the output of an instrument, a certification establishes traceability of a transfer standard to a NIST-traceable standard, and a verification establishes comparability of a standard to a NIST-traceable standard of equal rank.

The Standards Laboratory also certifies and calibrates on a quarterly basis the instruments used by the ARB's QAS auditors. Table 1 shows the types of services and volume for 2005. Information about the Standards Laboratory and the services that they provide is available at <http://www.arb.ca.gov/aaqm/qmosprog/stdslab/stdslab.htm>.

Table 1. Standards Laboratory Services Provided for 2005

| Service Provided | Number Conducted |
|---------------------------------|------------------|
| Ozone Certifications | 89 |
| Ozone Verifications | 18 |
| Ozone Calibrations | 0 |
| Low Flow Certifications | 295 |
| Low Flow Verifications | 0 |
| Low Flow Calibrations | 25 |
| High Flow Certifications | 48 |
| Ambient Gas Cylinders Certified | 73 |
| Source Gas Cylinders Certified | 119 |



V. LABORATORY AND FIELD STANDARD OPERATING PROCEDURES

Laboratory and field standard operating procedures (SOPs) are guidance documents for the operation of quality assurance programs used by the ARB, local districts and private industry. The SOPs are intended for field operators and supervisors; laboratory, data processing and engineering personnel; and program managers responsible for implementing, designing, and coordinating air quality monitoring projects. Each SOP has a specific method that must be followed to produce data-for-record. The SOPs are developed and published to ensure that, regardless of the person performing the operation, the results will be consistent. Most of the SOPs are available on the Internet at <http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.htm>.



VI. SITING EVALUATIONS

To generate accurate and representative data, air monitoring stations should meet specific siting requirements and conditions. It is assumed that the stations met the siting criteria in place at the time initial operation began. As such, non-conformance today is the result of changing regulations, or changes in surrounding conditions and land use. The siting requirements of the ARB's Quality Assurance Manual Volume II; 40 CFR 58, Appendix E; U.S. EPA's Quality Assurance Handbook Volume IV: U.S. EPA's Prevention of Significant Deterioration (PSD); and U.S. EPA's PAMS guidelines, present siting criteria to ensure the collection of accurate and representative data.

The siting criterion for each pollutant varies depending on the pollutant's properties, monitoring objective and intended spatial scale. The U.S. EPA's siting criteria are stated as either "must meet" or "should meet". According to 40 CFR 58, Appendix E, the "must meet" requirements are necessary for high quality data. Any exception from the "must meet" requirements must be formally approved through the Appendix E waiver provision. The "should meet" criteria establish a goal for data consistency.

Siting criteria are requirements for locating and establishing stations and samplers to meet selected monitoring objectives, and to help ensure that the data from each site are collected uniformly. There are four main monitoring objectives: to determine highest concentrations expected to occur in the area covered by the network; to determine representative concentrations in areas of high population density; to determine the impact on ambient pollution levels of significant sources or source categories; and to determine general background concentration levels. Typical siting designations are: micro, middle, neighborhood, and regional. These designations represent the size of the area surrounding the monitoring site which experiences relatively uniform pollutant concentrations. Typical considerations for each of these site designations are, for example, the terrain, climate, population, existing emission sources, and distances from trees and roadways.

Siting evaluations are conducted annually by QAS. Physical measurements and observations include probe/sensor height above ground level, distance from trees, type of ground cover, residence time, obstructions to air flow, and distance to local sources, are taken to determine compliance with 40 CFR Part 58, Appendix E requirements. If a criteria deficiency is found during a site evaluation, the site operator will be informed and an AQDA may be issued. For siting criteria distances, please refer to Appendix C.

VII. PROGRAM CONTACTS

| Program | Contact | Phone | Email |
|--------------------------|-----------------|----------------|---------------------|
| Gaseous Pollutant | Don Fitzell | (916) 322-3892 | Dfitzell@arb.ca.gov |
| Particulate Matter | Don Fitzell | (916) 322-3892 | Dfitzell@arb.ca.gov |
| Toxic Air Contaminants | Leena Janda | (916) 323-1439 | Hjanda@arb.ca.gov |
| Non-Methane Hydrocarbons | Patrick Rainey | (916) 327-4756 | Prainey@arb.ca.gov |
| Dioxins | Don Hammond | (916) 322-5924 | Dhammond@arb.ca.gov |
| Asbestos | Rebecca Neumann | (916)324-1145 | Rneumann@arb.ca.gov |
| Consumer Products | Don Fitzell | (916) 322-3892 | Dfitzell@arb.ca.gov |
| Meteorology | Don Fitzell | (916) 322-3892 | Dfitzell@arb.ca.gov |

APPENDIX A

AIR MONITORING NETWORK SURVEY

Quality Assurance Section
Monitoring and Laboratory Division





Gaseous Criteria Pollutant Monitoring as of December 31, 2005

| Parameter Measured | Ozone | Nitrogen Dioxide | Carbon Monoxide | Sulfur Dioxide | Hydrogen Sulfide* |
|---------------------------|--|-----------------------------|------------------------------------|---|---|
| Sampling Schedule | Continuous hourly average | | | | |
| Number of ARB Sites | 37 | 17 | 13 | 3 | 0 |
| Number of District Sites | 140 | 88 | 69 | 33 | 12 |
| Number of Sites in Mexico | 8 | 8 | 8 | 3 | 0 |
| Method Used By ARB | Ultraviolet photometry | Gas phase chemiluminescence | Non-dispersive infrared photometry | Ultraviolet fluorescence detector | Thermal oxidizer with ultraviolet fluorescence detector |
| EPA Reference Method | Ultraviolet photometry | Gas phase chemiluminescence | Non-dispersive infrared photometry | Spectrophotometry (pararosaniline method) | Not applicable |
| Data Availability | Planning and Technical Support Division, Air Quality Data Branch, (916) 322-6076; U.S. EPA Air Quality System (AQS) | | | | |

*Hydrogen sulfide is only a State criteria pollutant. A Federal standard has not been set.



Particulate Matter Monitoring as of December 31, 2005

| Parameter Measured | PM10 (0 - 10 microns) | | PM2.5 | |
|---|--|---|--|--|
| | Mass* | Nitrate, sulfate, chloride, ammonium, potassium | Mass (fine)** | Speciated |
| Sampling Schedule | Every 6 days (24-hr. samples), TEOM & BAM (continuous 24-hr.), (Ag. burn sites every 3 days from Sep. to Nov.) | | Every 3 days, BAM (continuous 24-hr.) (Bakersfield & Fresno-First sites every day) | 1 in 6 days |
| ARB Collection Method | High volume selective size inlet sampler | | Mass sequential, single channel & continuous | Speciation air sampling system (SASS) |
| Sampling Media | Quartz microfiber filter - 8 x 10 inch, BAM - filter tape, Teflon filter - 46.2 mm | | Teflon filter - 46.2 mm, BAM - filter tape | Teflon, nylon & quartz filter - 46.2 mm |
| Number of Sites Operated by the ARB | 34* (includes 12 sites in Mexico) | 7 (includes 1 site in Mexico) | 25** (Includes 2 sites in Mexico) | 7 |
| Number of ARB Collocated Sites | 2 | 1 | 6 | 1 |
| Additional Sites Analyzed by other Agencies | 14 BAAQMD* 25 SCAQMD* 6 SDAPCD* 94 other* | 17 SCAQMD 14 BAAQMD 1 SJVUAPCD | 72** | 17*** |
| ARB Analysis Method | Method 016 Electronic analytical balance | Method 007 & Method 023 ion chromatography | Method 055 Electronic analytical balance | Method 055 Electronic analytical balance Method 014 X-ray fluorescence Method 062 Filter preparation Method 064 Ion chromatography Method 065 Thermal/optical carbon |
| Laboratory Analyst | Scott Randall | Roxanna Walker | Mike Humenny | George Dunstan |
| Data Availability | Planning and Technical Support Division, Air Quality Data Branch, (916) 323-4887; U.S. EPA Air Quality System (AQS) | | | |

*These figures also include sites where PM10 mass is monitored using low-vol. method or continuously (1-hr. averages) using TEOM or BAM.

**These figures also include sites where PM2.5 mass is monitored continuously (1-hr. averages) using BAM.

***Analysis performed by U.S. EPA or SCAQMD laboratory.



Organic Toxic Air Contaminant Monitoring as of December 31, 2005

| Parameter Measured | Volatile Organic Compounds (VOCs) | | |
|---|--|--|---|
| | Aromatic & halogenated Compounds* | Oxygenates and Nitriles** | Ethanal (acetaldehyde) Methanal (formaldehyde) Butanone (methyl ethyl ketone) |
| Sampling Schedule | Every 12 days (24-hr. samples) | | |
| ARB Collection Method | XonTech 910A gaseous sampler | | XonTech 920 toxic air contaminant sampler |
| Sampling Media | Polished stainless steel canister | | DNPH-coated silica cartridges |
| Number of Sites Analyzed by the ARB | 19 (2 in Mexico) | | 21 |
| Number of ARB Collocated Sites | 4 (Bakersfield, Rubidoux) | | 2 (Bakersfield, Stockton) |
| Additional Sites Analyzed by other Agencies | 18 BAAQMD | | 0 |
| ARB Analysis Method | Method 058 Cryogenic trap preconcentration capillary GC/MS | Method 066 Cryogenic trap preconcentration capillary GC/PID | Method 022 High performance liquid chromatography/ultraviolet detector |
| Laboratory Analyst | Ferry Niyati, Ben Chang, Nati Lapurga, Vince Scola, John Medina | | Paul Chima |
| Data Availability | Planning and Technical Support Division, Air Quality Data Branch(916) 322-4887; U.S. EPA Air Quality System (AQS) | | |

*Dichloromethane, trichloromethane, tetrachloromethane, 1,1,1-trichloroethene, tetrachloroethene, benzene, toluene, styrene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, o-xylene, m/p-xylene, ethylbenzene, and 1,3-butadiene.

** Acrolein, Acetone, Acetonitrile, Acrylonitrile.



Hydrocarbon Monitoring as of December 31, 2005

| Parameter Measured | Non-methane hydrocarbon compound (NMHC) | | Continuous non-methane hydrocarbons | Carbonyl compounds |
|---|--|---|---|---|
| | Total NMHC | Speciated NMHC (69 species, C2 through C12) | | Acetone formaldehyde acetaldehyde |
| Sampling Schedule | Every 3 days, July through September plus episodes (3-hr. samples) | | Continuous hourly average | 3-hr. sample |
| ARB Collection Method | XonTech 910A gaseous sampler with XonTech 912 multi-sampler | | Thermal environmental (TECO) 55C hydrocarbon analyzer | XonTech 925 or other carbonyl sampler |
| Sampling Media | Polished stainless steel canister | | Not applicable | DNPH-coated silica gel cartridges |
| Number of Sites Analyzed by the ARB | 2 | | 4 | 0 |
| Additional Sites Analyzed by other Agencies | 6 SCAQMD (includes 2 continuous GC) 4 San Diego County APCD 4 San Joaquin Valley APCD 6 Ventura County APCD | | 14 | 4 SCAQMD 2 San Diego County APCD 2 San Joaquin County APCD 1 Ventura County APCD |
| ARB Analysis Method | Method 024 Cryofocusing direct GC/FID | Method 032 Cryofocusing GC/FID | Flame ionization detector | Method 022 High performance liquid chromatography/ultraviolet detector |
| Laboratory Analyst | Sean Roy | Sean Roy, Barry Taylor | Not Applicable | Paul Chima |
| Data Availability | Planning and Technical Support Division, Air Quality Data Branch, (916) 322-6076; U.S. EPA Air Quality System (AQS) | | | |



Meteorological Monitoring as of December 31, 2005

| Parameter Measured | Wind Speed | Wind Direction | Ambient Temperature | Relative Humidity | Atmospheric Pressure | Solar Radiation |
|--------------------------|--|-------------------------|--------------------------------------|---------------------|----------------------|---------------------------|
| Sampling Schedule | Continuous hourly average | | | | | |
| Number of ARB Sites | 38 | 38 | 38 | 15 | 18 | 4 |
| Number of District Sites | 146* | 146 | 123 | 64 | 36 | 42 |
| Number of Mexico Sites | 8 | 8 | 8 | 0 | 0 | 0 |
| Method Used by ARB | Propeller or cup anemometer | Wind vane potentiometer | Aspirated thermocouple or thermistor | Thin film capacitor | Pressure transducer | Thermopile or pyranometer |
| Data Availability | Planning and Technical Support Division, Air Quality Data Branch(916) 322-4887; U.S. EPA Air Quality System (AQS) | | | | | |

*Includes 3 vertical wind speed sensors.



TSP and Visibility Monitoring as of December 31, 2005

| Parameter Measured | Total Suspended Particulates (TSP) | | Coefficient of Haze | Relative Visibility |
|---|--|---|---|--|
| | Lead | Sulfate | Particulates | Light Scatter |
| Sampling Schedule | Every 6 days (24-hr. samples) | 1 every 12 days 4 every 6 days 2 every 3 days (24-hr. samples) | 2-hr. average | Continuous hourly average |
| ARB Collection Method | High volume total suspended particulate sampler | | Optical test tape sampler | Nephelometer |
| Sampling Media | Glass fiber filter 8 x 10 inch | | Filter tape | Not applicable |
| Number of Sites Analyzed by the ARB | 2 (Includes 1 site in Mexico) | 0 | 2 | 1 |
| Number of ARB Collocated Sites | 0 | 0 | 0 | 0 |
| Additional Sites Analyzed by other Agencies | 10 SCAQMD | 15 SCAQMD | 1 | 3 |
| ARB Analysis Method | Method 105 Graphite furnace atomic absorption/ZEEMAN | Method 033 Ion chromatography | Light transmittance through a filter tape | Scattering coefficient of light by suspended particles |
| Laboratory Analyst | Peter Samra | Roxanna Walker | Not applicable | Not applicable |
| Data Availability | Planning and Technical Support Division, Air Quality Data Branch(916) 322-4887; U.S. EPA Air Quality System (AQS) | | | |



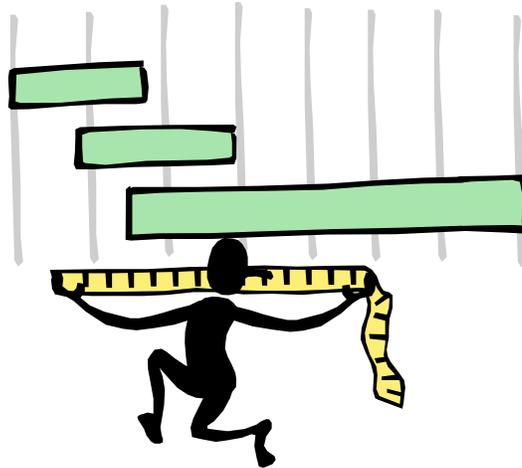
Toxic Metals Monitoring as of December 31, 2005

| Parameter Measured | Toxics Metals | |
|---|--|----------------------------------|
| | Al, As, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, Hg, K, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Ti, U, V, Y, Zn, Zr | Chromium VI |
| Sampling Schedule | Every 12 days (24-hr. samples) | |
| ARB Collection Method | XonTech 920 toxic air contaminant sampler | |
| Sampling Media | Teflon filter - 37 mm | Cellulose filter - 37 mm |
| Number of Sites Analyzed by the ARB | 23 (2 in Mexico) | 23 (2 in Mexico) |
| Number of ARB Collocated Sites | 2 (Bakersfield, Stockton) | 2 (Bakersfield, Stockton) |
| Additional Sites Analyzed by other Agencies | 0 | 0 |
| ARB Analysis Method | Method 034 X-ray fluorescence | Method 039 Ion chromatography |
| Laboratory Analyst | Mike Humenny | Samantha Scola |
| Data Availability | Planning and Technical Support Division, Air Quality Data Branch(916) 322-4887; U.S. EPA Air Quality System (AQS) | |

APPENDIX B

SITING CRITERIA DISTANCES

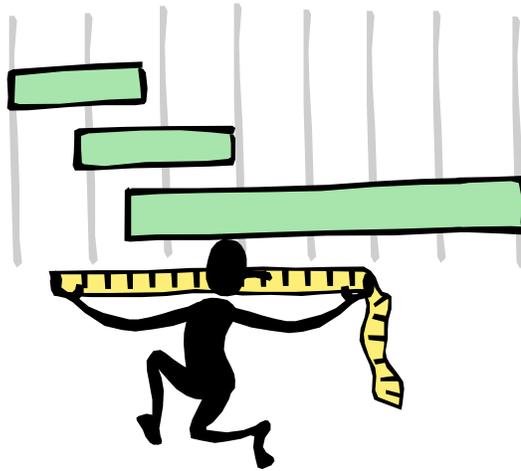
Quality Assurance Section
Monitoring and Laboratory Division



APPENDIX C

ARB's INSTRUMENT CONTROL LIMITS

Quality Assurance Section
Monitoring and Laboratory Division



Instrument/Sensor Control Limits

ARB's Control and Warning Limits

| <u>Limits</u> | | <u>Instrument</u> |
|----------------------------|------------------------|--|
| <u>Control</u> ±15% | <u>Warning</u> ±10% | All Gaseous Criteria and Non-Criteria Analyzers |
| ±15% | ±10% | Total Suspended Particulate (TSP) Samplers |
| ±10% | ±7% | PM ₁₀ , Dichotomous (Dichot), Lead (Pb), Tapered Element Oscillating Microbalance (TEOM), Toxic Air Contaminant (XonTech 920) Samplers, Beta Attenuated Monitors (BAM), and Carbonyl (XonTech 925) Samplers |
| ±4% (Flow) ±5% (Design) | None None | PM _{2.5} |
| ±20% | None | Laboratory Audits (Toxics, PAMS, Motor Vehicle Exhaust, and Total Metals) |

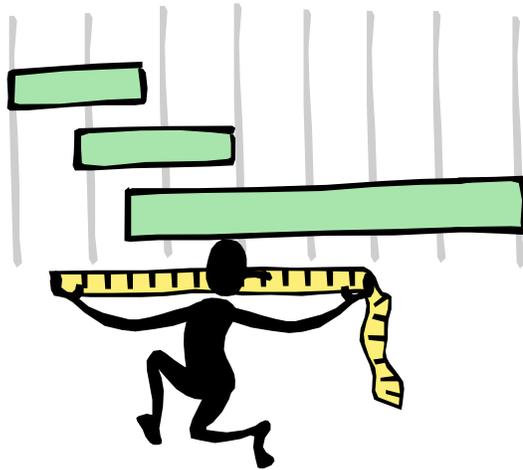
Acceptance Criteria For Meteorological (MET) Sensors

| <u>Limits</u> | <u>Sensor</u> |
|--|--|
| ±1.0° Celsius (±0.5°C PAMS only) | Ambient Temperature |
| ±2.25mm of Mercury (Hg) | Barometric Pressure |
| ±3%RH for 10-90%RH ±5%RH for <10 or >90%RH | Relative Humidity |
| ±5% Watts/m ² | Solar Radiation |
| less than or equal to 5° combined accuracy and orientation error | Wind Direction |
| less than or equal to 0.5m/s | Wind Direction Starting Threshold |
| ±0.25m/s between 0.5 and 5m/s and less than 5% difference above 5m/s | Horizontal Wind Speed |
| less than or equal to 0.5m/s | Horizontal Wind Speed Starting Threshold |
| ±0.25m/s between 0.5 and 5m/s and less than 5% difference above 5m/s | Vertical Wind Speed |
| less than or equal to 0.5m/s | Vertical Wind Speed Starting Threshold |

APPENDIX D

REFERENCES

Quality Assurance Section
Monitoring and Laboratory Division



References

1. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume I. Principles, EPA-600/9-76-005, January 1984.
2. Quality Assurance Handbook for Air Pollution Measure Systems. Volume II. Ambient Air Specific Methods, EPA-600/4-77-027a, May 1977.
3. State and Local Air Monitoring Network Plan, California Air Resources Board, May 1993.
4. Code of Federal Regulations, Title 40, Protection of the Environment, Part 58, Ambient Air Quality Surveillance (July 1992).
5. Air Monitoring Quality Assurance Manual. Volume I. Quality Assurance Plan, Monitoring and Laboratory Division, California Air Resources Board, February 1995.
6. Strategic Plan, California Air Resources Board, 1997.
7. Technical Assistance Document for Analysis of Ozone Precursors (TAD), September 30, 1998.