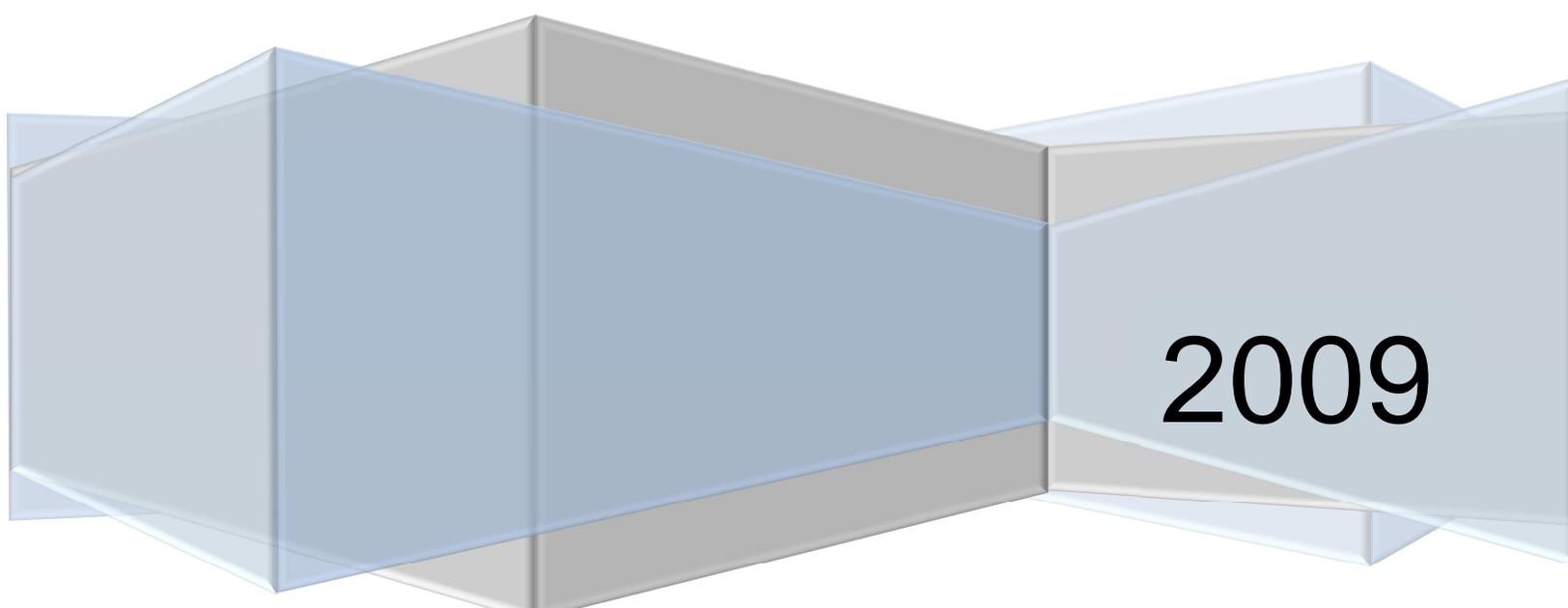


**California Environmental Protection Agency
Air Resources Board**

Data Quality Report

**Monitoring and Laboratory Division
Quality Assurance Section**



2009

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2009

Annual Data Quality Report

for
the Monitoring and Laboratory Division
and
Local Districts' Air Monitoring Networks

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Air Resources Board
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Quality Assurance Section

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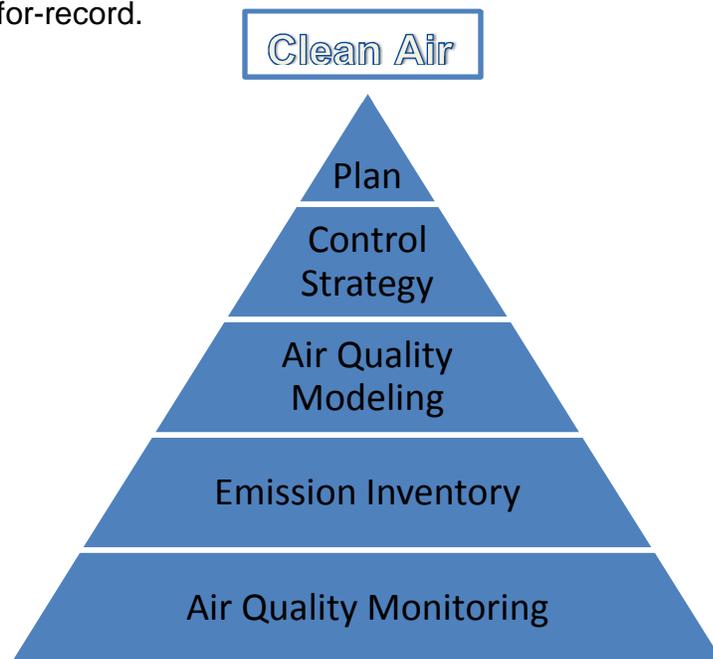
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I. INTRODUCTION

The purpose of this report is to provide ambient air quality data users with a summary of the quality of the 2009 ambient data in quantifiable terms. This is the tenth 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.

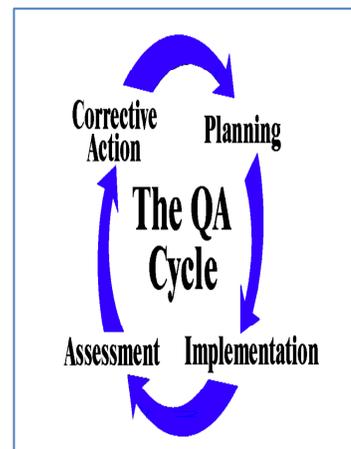
The California Air Resources Board's (ARB) mission is to promote and protect public health, welfare, and ecological resources through effective and efficient reduction of air pollutants while recognizing and considering the effects on the economy of the State. The Monitoring and Laboratory Division (MLD) 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. Mandated by State law, MLD 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, motor vehicle exhaust, asbestos, consumer products and meteorological parameters. Data from these monitoring sources provide the foundation to determine the nature of the pollution problem and assess the effectiveness of the control measures and programs. MLD's 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 U.S. EPA and can be considered good quality data and data-for-record.

Good quality data or data-for-record collected by the ambient air network and MLD lays the foundation for rulemaking and policy decision for the future. As the diagram to the right illustrates, the data analyzed and collected by MLD is utilized in developing ARB's multiple emissions inventory databases. These data bases include, but are not limited to: Air Quality System (AQS) the federal emissions database, Air Quality Data Statistics (ADAM) which allows patrons to view year-to-year trends and configure data to the specific needs of the user; and Air Quality and Meteorological Information System (ADMIS) which provides the public real time emission



levels throughout the state. These emission inventory databases combined with several others collectively provide the groundwork for modeling, planning and ultimately policy making and regulations. Additional information for ADAM and AQMIS can be found at <http://www.arb.ca.gov/adam/> and <http://www.arb.ca.gov/aqm2/aqm2.php>, respectively.

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 main 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, which includes conducting regular performance audits, on-site system audits interlaboratory comparisons, and periodic evaluations of internal quality control data.

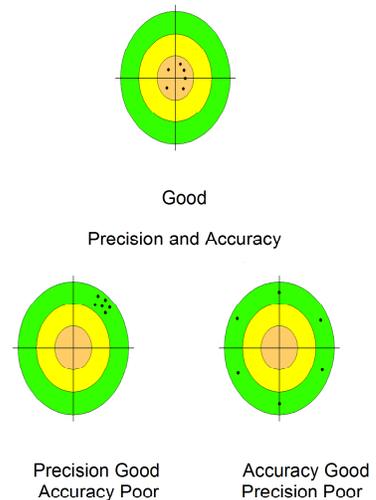
II. QUALITY CONTROL AND QUALITY ASSESSMENT

QAS supports all ambient monitoring programs undertaken by MLD, which in 2009 included gaseous pollutants, particulate pollutants, toxic air contaminants, pesticides, dioxin/furans and meteorological sensors operated by ARB and local and private air monitoring agencies. There are approximately 260 air monitoring sites in 15 separate air basins operating in California.

Information about each air monitoring station audited by ARB is available at <http://www.arb.ca.gov/qaweb/>. The website 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 provides access to District precision and accuracy reports. These reports are available on a limited basis to District staff.

The assessment of an ambient air monitoring system consists of several components, including but not limited to data representativeness, ambient data completeness, and data coverage of the ambient air samples collected at individual sites. Information about these data sets can be found in many locations, for example, considerations of ambient data for assessing the attainment of the State 8-hour ambient ozone standard can be found at <http://www.arb.ca.gov/regact/area06/apppe.pdf>. The focus of this report, however, is on the quality and precision of the ambient air data.

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. This figure demonstrates the importance of having good precision and accuracy for ensuring good data quality. Data that must meet specific requirements (i.e., criteria pollutants) are referred to as *controlled data sets*. Criteria for the precision and accuracy 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, instrument maintenance logs, and/or audit results. After an AQDA has been issued, the data in question can be affected in three ways: invalidated, corrected or released. Invalidated data is flagged and is considered not for record; meaning, the data set will not be utilized in any designation, enforcement or regulatory decisions. Corrected data pertains to when a calculated correction value is applied to the existing data set allowing the data to meet the established control criteria. Released data sets meet compliance criteria and can be used in all aspects of decision making. The result of the Districts' investigation will determine which method will be applied to the specific data set in question. The District must confirm that an analyzer/sampler has operated within ARB's

control limits of (+/-10 percent for ozone and +/-15 percent for all other gaseous, +/-10 percent for PM10 and +/-4 percent for PM2.5), or for siting or temperature conditions. Otherwise, the respective agency must take corrective action.

Data without formal data quality objectives (e.g., 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.

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 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), ozone (O₃), nitrogen dioxide (NO₂), 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 arithmetic mean of 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. The minimum and maximum are included to convey the range in the percent differences.

Overall, the responses of the individual analyzers indicate that as a whole, the network is providing accurate data. The most common causes for audit failure are malfunctions within the instrument and leaks in the sampling system. Table A1 summarizes the 2009 performance audit results for the gaseous criteria pollutants.

Table A1. 2009 Results for Criteria Pollutants Performance Audits Conducted by ARB

Pollutant	Number of Samplers Audited	Number of AQDAs	Days of Data loss	Average percent Difference	95% LL	95% UL	Minimum	Maximum
CO	43	0	0	0.9	-4.7	6.4	-6.5	6.9
O3	124	4	0	-1.1	-8.2	5.9	-13.9	8.9
NO2	69	2	7	-3.7	-10.8	3.4	-14.2	6.5
SO2	21	0	0	0.8	-0.5	2.1	0.0	2.5
H2S	7	0	0	-6.6	-13.5	0.3	-11.8	-2.6

Source: Quality Assurance Section, Accuracy Estimates

Precision (field): Precision checks (zero and span) are performed by site operators 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 measurements is computed as the precision of that instrument's measurements.

In October 2006, U.S. EPA adopted new rules in Title 40, Code of Federal Regulation Part 58 Appendix A regarding the use of the precision and accuracy data in achieving the data quality objectives. For precision, the new statistic is the upper bound of the coefficient of variation (CV), which reflects the highest tolerable variability in the data. It is important to note that the U.S. EPA has not changed the types of samples used to assess precision; rather, the agency changed the statistic used to evaluate it.

Under the new rule, the CV upper bound is not to exceed 7 percent for ozone or 10 percent for other pollutants. Below is a discussion of the results in California for 2009 in each of the four Primary Quality Assurance Organizations (PQAOs). The PQAOs in California include: the Bay Area Air Quality Monitoring District, South Coast Air Quality Monitoring District, San Diego Air Pollution Control District, and CARB.

For gaseous pollutants (CO, NO₂, O₃, and SO₂), all PQAOs met the 7 percent or 10 percent CV criteria in 2009. That is, all sites in California showed the upper bound for the CV to be less than 7 percent for ozone and less than 10 percent for the other gases, as shown in Table A2 below. Information for years 2007 and 2008 are provided for historical perspectives. In general, 2009 precision data are consistent with the previous two years.

In addition, ARB has set a goal of 85 percent for capturing ambient data (Volume I, Quality Assurance Plan). Consistent with this goal, MLD has set 85 percent as the minimum target for precision data collection. This target was achieved at most stations in California. Table A2 summarizes the number of sites with less than 85 percent of the required precision data reported for 2009.

Table A2. 2007-2009 Precision Data Completeness Results

<i>Pollutant</i>	<i>PQAO</i>	<i>Year</i>	<i># Sites with less than 85 % precision data</i>	<i>Coefficient of Variation Based on Reported Sites</i>
Carbon Monoxide	Bay Area	2007	0	1.70
		2008	0	1.89
		2009	0	2.00
	CARB	2007	1	3.25
		2008	1	3.75
		2009	1	4.72
	San Diego	2007	0	4.27
		2008	0	2.74
		2009	0	2.83
	South Coast	2007	1	4.14
		2008	1	3.90
		2009	0	2.83
Nitrogen Dioxide	Bay Area	2007	0	1.73
		2008	0	1.82
		2009	0	2.02
	CARB	2007	1	5.46
		2008	2	5.72
		2009	1	5.73
	San Diego	2007	0	4.68
		2008	0	4.12
		2009	1	3.86
	South Coast	2007	2	5.39
		2008	3	5.71
		2009	0	4.99

Ozone	Bay Area	2007	0	1.25
		2008	0	1.41
		2009	0	1.19
	CARB	2007	1	4.12
		2008	0	4.49
		2009	1	4.39
	San Diego	2007	0	2.73
		2008	0	3.01
		2009	0	2.24
	South Coast	2007	1	3.82
		2008	2	3.74
		2009	0	3.04
Sulfur Dioxide	Bay Area	2007	0	1.10
		2008	0	1.15
		2009	0	1.35
	CARB	2007	1	5.62
		2008	2	4.58
		2009	1	4.27
	San Diego	2007	0	3.01
		2008	0	3.51
		2009	0	4.53
	South Coast	2007	0	5.97
		2008	0	4.17
		2009	0	4.79

Source: Air Quality System, AMP 255 Data Quality Report

B. Particulate Matter



Particulate Samplers

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 lungs and contain substances that are particularly harmful to human health. Respirable particulate matter (PM₁₀) and fine particulate matter (PM_{2.5}) 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 PM_{2.5}. 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>.

Accuracy (field): The accuracy of particulate samplers is determined by comparing the instrument's flow rate to a certified orifice (PM₁₀, TSP, and PM_{2.5} 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, 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 arithmetic mean of 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. The minimum and maximum are included to convey the range in the percent differences. Table B1 summarizes the 2009 performance audit results for the particulate samplers. Overall, the flow audit results indicate that the flow rates of samplers in the network are almost all within ARB control limits of +/-10 percent for PM₁₀, +/-4 percent for PM_{2.5} and +/-15 percent for TSP. The TSP data accuracy estimates include samplers that analyze for mass and/or sulfates and/or lead.

Table B1. 2009 Results for Particulate Sampler Performance Audits Conducted by ARB

Pollutant	Number of Samplers Audited	Number of AQDAs	Average percent Difference	Days of Data Lost	95% LL	95% UL	Minimum	Maximum
PM2.5	68	2	0.0	441	-3.2	3.1	-3.5	3.7
PM10	100	2	-0.2	35	-5.3	5.0	-11.2	5.3
PM10 Partisol	4	0	0.6	27	-1.9	3.1	-1.2	1.8
TEOM	12	0	-1.2	0	-9.8	7.4	-8.7	9.5
BAM PM10	9	0	-0.5	0	-7.4	6.4	-8.5	3.7
BAM PM2.5	66	2	0.0	101	-3.2	3.2	-4.6	3.1
TSP	6	0	-0.4	55	-14.0	13.1	-8.5	10.3

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 select sites and are intended to represent the overall network precision. Validity of the data is based on the percent difference of the mass concentrations of the two samplers.

In October 2006, U.S. EPA adopted new rules in Title 40, Code of Federal Regulation Part 58 Appendix A, regarding the use of the precision and accuracy data in achieving the data quality objectives. For precision, the new statistic is the upper bound of the coefficient of variation (CV), which reflects the highest tolerable variability in the data. Under the new rule, the CV upper bound is not to exceed 10 percent for particulate matter. When a monitor exceeds requirements, a sequence of actions is initiated. The PQAO or the District investigates the exceedance and corrective action is taken, which may lead to the invalidation of the ambient data collected in the relevant periods.

At low concentrations, agreement between the measurements of collocated samplers may be relatively poor. For this reason, collocated measurement pairs are selected for use in the precision calculations only when both measurements are equal to or above the following limits: (1) TSP: 20 µg/m³; (2) Pb: 0.02 µg/m³; (3) PM10(Hi-Vol): 15 µg/m³; (4) PM10(Lo-Vol): 3 µg/m³; (5) PM10-2.5 and PM2.5: 3 µg/m³

In terms of meeting the required collocated sampling, Table B2 shows the number of sites required by U.S. EPA and the number with collocated precision data reported in respective years. In 2009, CARB did not meet the collocated sampling requirement for lead, PM10, and PM2.5 (Method 120), while South Coast and Great Basin did not meet the requirement for PM10, and Bay Area for PM2.5 (Method 145). Note that while Great Basin is not a PQAO, Table B2 provides information specific to this district to match the automatic report AMP255 from the U.S. EPA. In addition, each required

collocated sampling site must have at least 75 percent of the data reported to meet the federal precision completeness criterion, although ARB's goal is 85 percent. Table B4 also displays precision percent completeness and CV. Information for years 2007 and 2008 are provided for historical perspectives.

Based on the collocated data collected, the CV requirements were not met for lead (Pb) by the South Coast in 2009. For PM10, however, the CV was below 10 percent in the Bay Area, CARB, and San Diego. On the other hand, Great Basin did not meet the CV requirement for PM10. Results are mixed for PM2.5, with Bay Area sites meeting the 10 percent requirement and varying outcomes among CARB and San Diego sites. South Coast met the completeness criteria but exceeded the CV requirement. Note that Great Basin did not meet the requirements in 2009 for PM2.5.

Compared to 2007 and 2008 results, precision statistics were fairly consistent in 2009 for most PQAOs and pollutants, with the exceptions where the CV requirements were not met, as noted in the previous paragraph.

Table B2. 2007-2009 Precision results based on collected samplers

Pollutant	PQAO	Year	Method Code*	# Collocated Sites Required	# Collocated Sites Reported	% Precision Completeness Based on Reported Sites	Coefficient of Variation Based on Reported Sites
Lead	CARB	2007		1	0	0	N/A
		2008		1	0	0	N/A
		2009		1	0	0	N/A
	South Coast	2007		2	2	100	10.20
		2008		2	2	100	0.00
		2009		2	4	100	37.00
PM10	Bay Area	2007		2	2	100	3.99
		2008		2	2	100	4.30
		2009		1	1	100	2.75
	CARB	2007		16	9	94	5.25
		2008		14	7	95	4.71
		2009		13	7	100	4.04
	Great Basin	2007		2	1	18	16.20
		2008		2	1	23	20.63
		2009		2	1	42	22.42
	San Diego	2007		1	2	100	3.98
		2008		1	2	100	3.04
		2009		1	2	100	3.49
	South Coast	2007		3	3	100	10.80
		2008		4	3	100	8.39
		2009		4	3	100	5.14
PM2.5	Bay Area	2007	117	1	0	0	N/A
		2008	117	1	1	33	4.65
		2009	117	1	1	100	5.79
		2007	120	2	1	97	5.16
		2008	120	2	1	80	7.77
		2008	145	2	1	13	5.67
		2009	145	2	1	65	7.58
		2009	170	1	1	100	18.57

PM2.5	CARB	2007	117	2	3	100	8.69
		2008	117	2	2	100	9.75
		2009	117	2	2	100	7.30
		2007	118	2	4	100	8.52
		2008	118	3	5	100	8.06
		2009	118	3	5	100	9.13
		2007	120	2	1	98	8.09
		2008	120	2	1	75	18.11
		2009	120	1	0	0	N/A
		2007	170	1	0	0	N/A
		2008	170	1	0	0	N/A
		2009	170	1	1	100	22.35
	Great Basin	2007	118	1	1	57	10.51
		2008	118	1	1	93	16.13
		2009	118	1	1	53	15.05
	San Diego	2007	118	1	1	100	10.78
		2008	118	2	2	60	5.92
		2009	118	2	2	88	9.57
		2007	120	1	1	100	4.13
		2008	120	1	0	0	N/A
		2008	170	1	0	0	N/A
South Coast	2007	120	3	3	100	7.59	
	2008	120	3	3	100	4.16	
	2009	120	3	3	100	5.17	
	2008	170	1	0	0	N/A	
	2009	170	1	2	100	13.61	

*Note: Method 117= R & P Model 2000 PM2.5 Sampler w/WINS; Method 118= R & P Model 2025 PM2.5 Sequential w/WINS; Method 120= Andersen RAAS2.5-300 PM2.5 SEQ w/WINS; Method 145= R & P Model 2025 PM-2.5 Sequential Air Sampler w/VSCC; Method 170= Met One BAM-1020 Mass Monitor w/VSCC. Red font indicates CV greater than 10% in 2009 while blue font indicates CV greater than 10% in 2007 or 2008.

Source: Air Quality System, AMP 255 Data Quality Indicator Report, run September 7, 2011

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 2009 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 except for one temperature sensor failure at Santa Barbara APCD.

Laboratory audits were also conducted for the PM10 ions program using NIST-traceable filter standards for nitrate (NO₃⁻), sulfate (SO₄⁻²), chloride (Cl⁻), ammonium (NH₄⁺), and potassium (K⁺). Audit results for the NLB ions program for 2009 were within the targeted +/-20 percent control limit established for the audit procedure. Laboratory audits for the TSP (Pb) program are also conducted using NIST-traceable standards. Due to limited resources, QAS was unable to conduct any lead (Pb) laboratory audits in 2009.

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 when 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 2009, 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-B4 show the unexposed and exposed filter replicate results for ARB's laboratory in 2009.

Table B3. 2009 Summary of ARB's Unexposed Filter Mass Replicates

QC Checks for Pre-weighed Filters	PM10	PM2.5
Total # samples analyzed	3660	3904
# of replicates	482	485
Percent replicated	13.2	12.4
# out-of-range	0	0

Source: Inorganics Laboratory Section, Quality Control Report

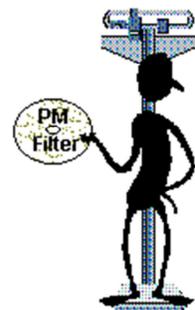


Table B4. 2009 Summary of ARB's Exposed Filter Mass Replicates

QC Checks for Post-weighed Filters	PM10	PM2.5
Total # samples analyzed	3103	3646
# of replicates	357	450
Percent replicated	11.5	12.2
# 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 public exposures to air toxic 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 2009: laboratory audits and a whole air comparison check.

Accuracy (field):

In 2009, 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. The canister is then sent to each participating laboratory for analysis. The laboratories follow their standard operating procedures in analyzing the contents and report their results to QAS for comparison. Results from the seven participating laboratories were consistent (See Figures C1). If any laboratory's response for a compound was not consistent with the other laboratory's responses, the laboratory was notified of the discrepancy.

Figure C1. (continued on the next page)

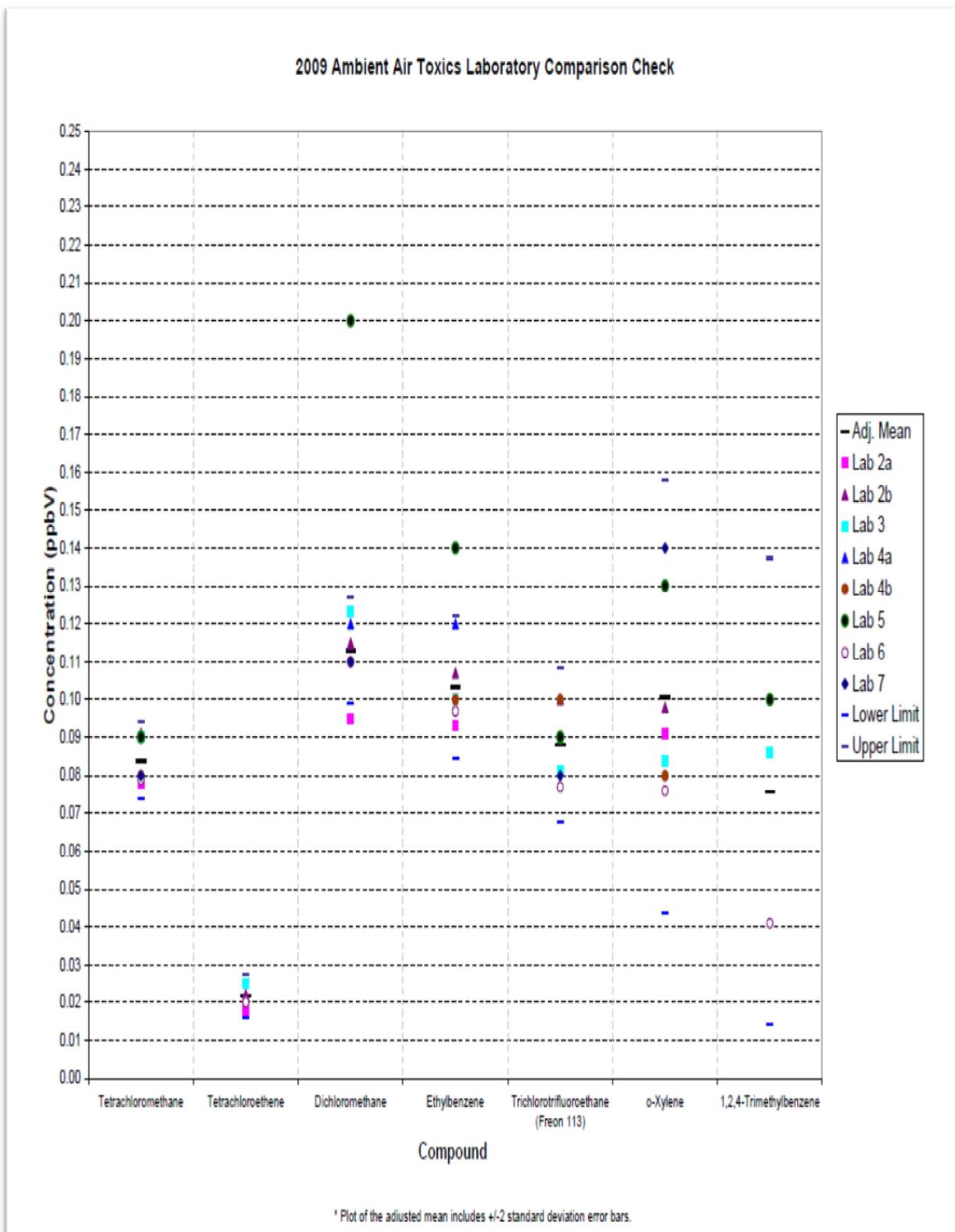


Figure C1. (continued on next page)

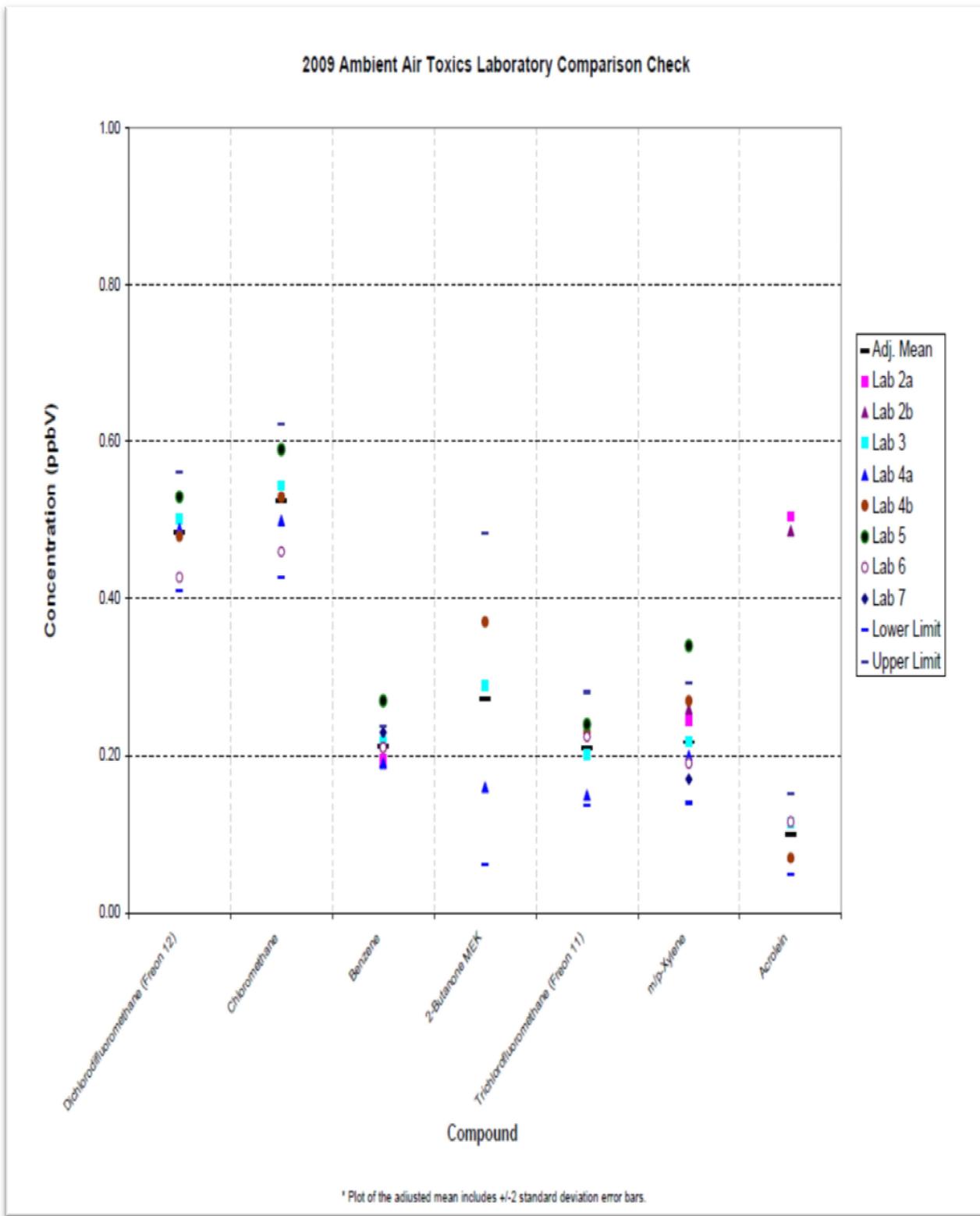
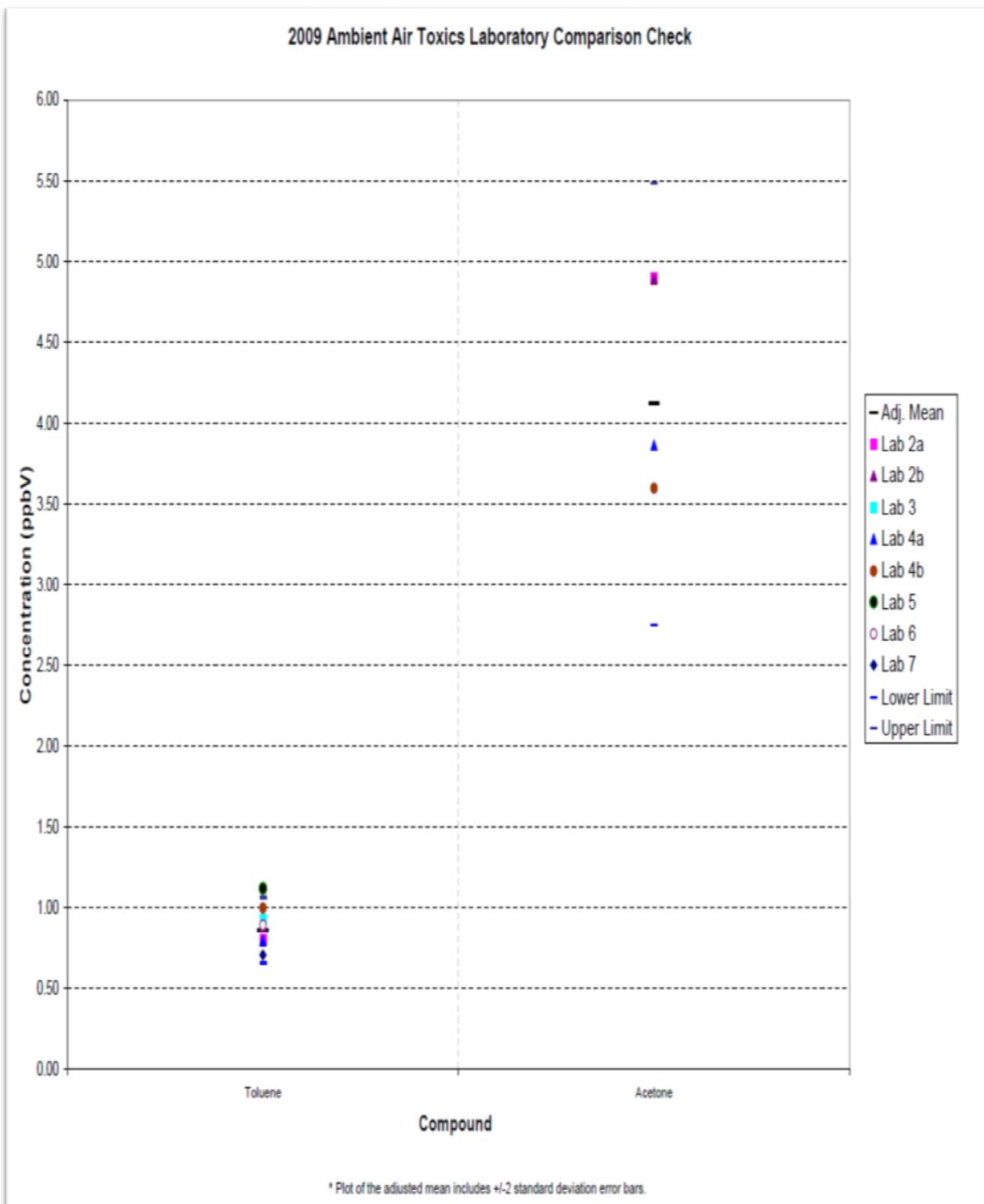


Figure C1. (continued from previous pages)



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.



Overall, the 2009 results indicate that the samplers maintained stable flows. 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.

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 analyzers' individual percent differences for all audit test levels at a single site. The minimum and maximum are included to convey the range in the percent differences.

Table C1. 2009 Results for Toxic Air Sampler Flow Rate Performance Audits Conducted by ARB

Pollutant	Number of Samplers Audited	Number of AQDAs	Days of Data Lost	Average Percent Difference	95% LL	95% UL	Minimum	Maximum
Hexavalent Chromium	17	0	0	-1.5	-6.8	3.9	-6.3	3.3
Total Metals	17	0	0	-1.4	-8.5	5.6	-9.5	3.4
Aldehydes	17	0	0	-0.9	-8.6	6.9	-6.8	9.4

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 differences presented in the table represents the average difference between the laboratory's measured value and the NIST certified value. The audit results for 2009 showed that all of the compounds were within ± 20 percent of the NIST certified values.

Table C2. ARB's 2009 Toxic Air Contaminants Laboratory Performance Audit Results

Compound	ARB Laboratory
	Percent Difference
Benzene	-0.4
Bromomethane	1.6
1,3-Butadiene	-1.5
Carbon Tetrachloride	0.0
Chloroform	-8.0
Dichlorodifluoromethane	-4.0
Trichlorofluoromethane	-1.7
Ethylbenzene	-2.9
Dichloromethane	-3.7
Perchloroethylene	-1.9
Styrene	-8.2
Toluene	-2.3
Trichloroethylene	0.0
Trichloroethane	-4.5
m/p-Xylene	-3.6
o-Xylene	-1.9
cis-1,3-Dichloropropane	-1.1
Trans-1,3-Dichloropropane	9.9

Precision (field and lab): As part of the 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 2009, 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 percent of the toxic samples. In 2009, all duplicate results with concentrations greater than five times the published levels of detection (LOD) 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 the 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 the compounds meet the cleanliness criteria.

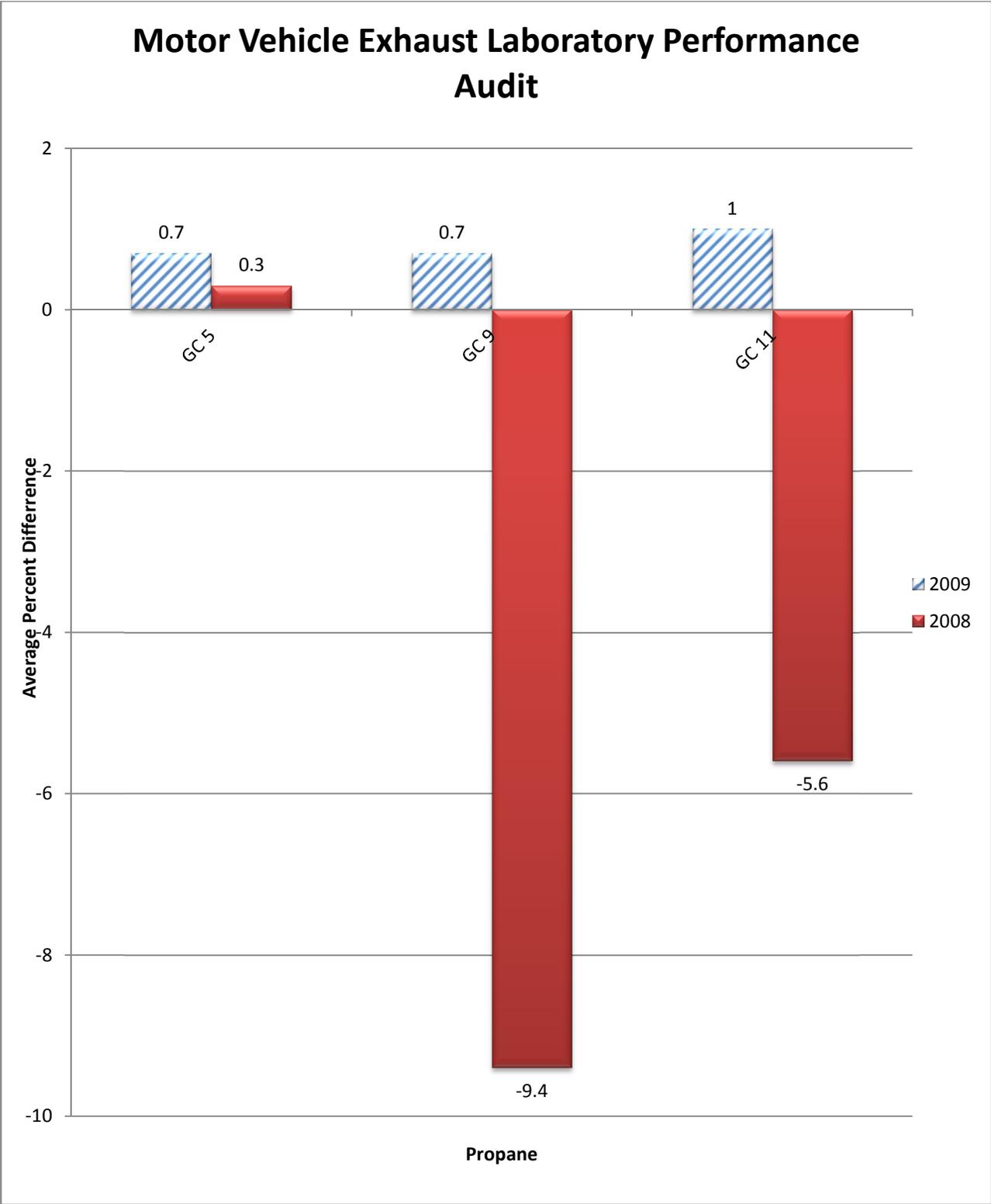
The toxics audit results, which serve to assure the validity of the toxics data, and several papers that discuss the elements of the QA program in detail are available at http://www.arb.ca.gov/aaqm/qmosqual/perfaudit/toxics/qa_toxic.htm.

D. Motor Vehicle Exhaust

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.

Accuracy: Laboratory performance audits are conducted annually of the Southern Laboratory Branch of ARB for components of motor vehicle exhaust, specifically propane. The laboratory results for 2008 and 2009 are shown in Figure D3. The performance audit results showed that the compound was within ARB's control limits of ± 20 percent.

Figure D3. 2008-2009 Motor Vehicle Exhaust Audit



E. Asbestos



Asbestos samplers

Asbestos is the name given to a group of six fibrous minerals that have been used for manufactured goods due to their tensile strength and heat-resistant properties. Naturally occurring asbestos (NOA) is present in California and is commonly associated with ultramafic and serpentine rocks which can be found in many parts of the State. When these rocks are broken or crushed, asbestos fibers may become airborne, and the public could be exposed.

Asbestos inhalation is associated with potentially lethal lung diseases such as mesothelioma, asbestosis, and lung cancer. In 1986, ARB identified naturally-occurring asbestos as a toxic air contaminant (TAC) and subsequently adopted two Airborne Toxic Control Measures (ATCM) to address prevention of public exposure to asbestos. The asbestos ATCMs prohibit the use of serpentine or ultramafic rocks containing ≥ 0.25 percent asbestos for unpaved surfacing materials and controls dust emissions from construction, grading, and surface mining in areas where ultramafic and serpentine rocks are present.

Test Method 435, entitled “Determination of Asbestos Content of Serpentine Aggregate,” was adopted in 1991 as the referenced test method for the Surfacing ATCM. It has also been used as a bulk method to determine asbestos content in rocks and soils. In 2007, the Operations Planning and Assessment Section (OPAS) of MLD conducted an interlaboratory study (ILS) to determine variability among laboratories using M435 to analyze asbestos content. The ILS concluded that variability in sample processing and analysis affected the percentage of asbestos reported from the same samples. Following two public asbestos workshops in 2008 on how to minimize such variability, OPAS sent out surveys to laboratories, consultants, and federal/state/district air quality regulators to solicit their comments.

In 2009, OPAS pulled together survey results, information from the ILS, consultation with other stakeholders, and the research of more than 30 other methods for asbestos analyses. As a result, OPAS identified possible changes to Test Method 435 and the asbestos ATCMs. OPAS presented these potential changes to other air quality regulators (i.e., EPA Technical Review Workgroup, California Department of Toxic Substances Control, local air districts), at professional meetings (i.e., Sacramento Association of Environmental and Engineering Geologists, 2009 Annual Meeting of the Geological Society of America), and to other consultants for further comments and suggestions.

OPAS put out a request for bid on a contract that would allow staff to test potential modifications to Test Method 435. A contract was signed in November 2009 and testing began shortly thereafter.

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

F. 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): QAS does not conduct performance audits on the Consumer Product Program at this time. The Special Analysis Section (SAS) 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 percent of the samples. The results from the analyses are compared, and the difference should be less than ± 3 percent. 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 ± 3 percent, 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.

SAS 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. Overall, in 2009 consumer products data met the establish control criteria. More information is available at <http://www.arb.ca.gov/enf/consprod.htm>.

G. Meteorology



Meteorological Tower

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. QAS audits according to those levels.

The wind speed, wind direction, barometric pressure and outside temperature data sets are controlled data sets, and subject to meeting ARB’s acceptance criteria, which can be found in Appendix B. Since the inception of the meteorological audit program, the data quality has improved significantly.

Accuracy (field): The accuracy of meteorological sensors are checked by annual performance audits. Table G1 summarizes the 2009 audit results. The average difference (average degree difference with respect to ambient temperature) represents the arithmetic mean of 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. The minimum and maximum are included to convey the range in the percent differences. Information about the meteorological monitoring program is available at <http://www.arb.ca.gov/aaqm/met.htm>

Table G1. 2009 Results for Meteorological Sensor Performance Audits Conducted by ARB

Sensor	Number of Audits	Number of AQDAs	Days of data lost	Average percent Diff	95% LL	95% UL	Minimum	Maximum
Ambient Temp	71	4	50	0.1	-0.3	0.5	-0.4	1.1
Wind Direction	72	4	252	0.1	-4.7	4.9	-9.7	10.6
Horizontal Wind Speed	76	2	0	0.3	-1.8	2.4	-1.1	4.4
Barometric Pressure	34	3	19	-0.3	-3.3	2.8	-3.3	4.9

Source: Quality Assurance Section, Accuracy Estimate

III. 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 verification establishes comparability of a standard to a NIST-traceable standard of equal rank.

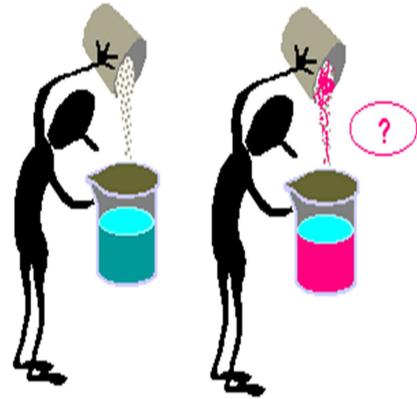
The Standards Laboratory also certifies and calibrates on a quarterly basis the instruments used by the ARB's QAS auditors. Table 1 shows the types of services and volume for 2009. Information about the Standards Laboratory is available at <http://www.arb.ca.gov/aaqm/qmosprog/stdslab/stdslab.htm>.

Table 1. Standards Laboratory Services Provided for 2009

Service Provided	Number Conducted
Ozone Certifications	35
Ozone Verifications	21
Low Flow Certifications	38
Low Flow Calibrations	38
Low Flow Verification	1
High Flow Certifications	34
Ambient Gas Cylinders Certified	81
Source Gas Cylinders Certified	7

IV. 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 ARB, local districts and private industry. 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>.



V. 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.

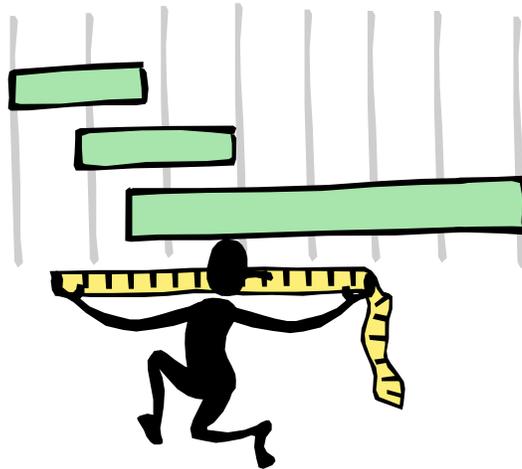
Siting criteria are requirements for locating and establishing stations and samplers to meet selected monitoring objectives, and to help ensure that the data from each site are collected uniformly. There are four main monitoring objectives: to determine highest concentrations expected to occur in the 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, or regional scale. 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 which 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 A.

APPENDIX A

SITING CRITERIA DISTANCES

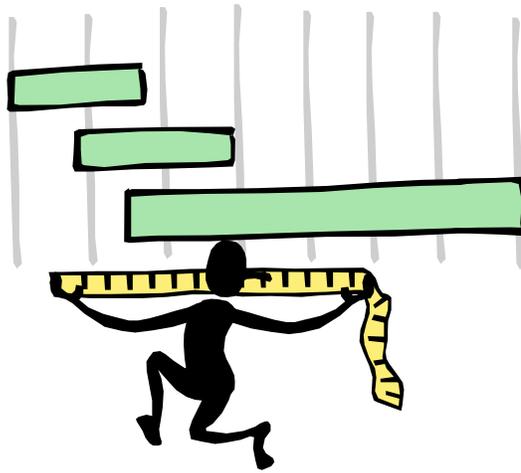
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APPENDIX B

ARB's INSTRUMENT CONTROL LIMITS

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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)

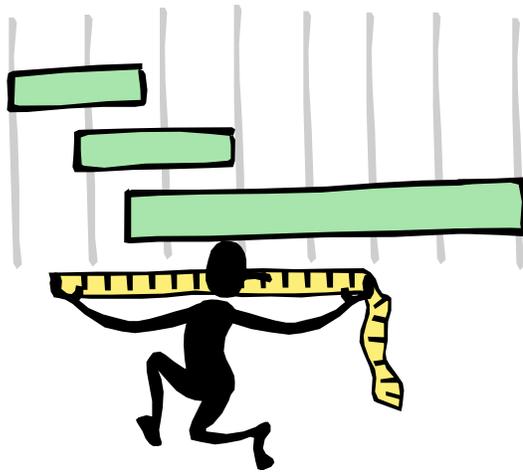
Acceptance Criteria For Meteorological (MET) Sensors

<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 C

REFERENCES

Quality Assurance Section
Monitoring and Laboratory Division



References

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2. Quality Assurance Handbook for Air Pollution Measure Systems. Volume II. Ambient Air Specific Methods, EPA-600/4-77-027a, May 1977.
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7. Technical Assistance Document for Analysis of Ozone Precursors (TAD), September 30, 1998.