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1. Quality Policy Statement and Concurrences

The Water Quality Laboratory (WQL) is a State of California certified environmental testing laboratory that provides services to the City of San Diego's Water Operations Division, to help ensure that the citizens of San Diego are provided with safe, high quality water, at a reasonable cost.

The Water Quality Laboratory is committed to supporting the quality assurance and quality control procedures as outlined in this Quality Assurance (QA) plan. These practices ensure that all data generated by the WQL are scientifically valid, legally defensible, and of known quality.

This Document utilizes the format and guidelines provided in: *The Certification of Environmental Laboratories*, CCR Title 22, Division 4, Chapter 19 and *Manual for the Certification of Laboratories Analyzing Drinking Water*, Fifth Edition, January 2005, EPA 815-R-05-004.

Concurrences:

(1) Name: Dana Chapin
Title: Water Quality Superintendent

Signature: _____ Date: _____

(2) Name: Donna Skinner
Title: Senior Chemist

Signature: _____ Date: _____

(2) Name: Judy Pawluczuk
Title: Quality Assurance Officer, Associate Chemist

Signature: _____ Date: _____

2. Purpose and Scope

This document describes the policies, objectives, principles, authority, responsibilities, implementation, and review of all data quality activities performed in the WQL. The goal is to ensure that all work performed in the WQL is planned, executed, and reviewed with quality assurance/quality control principles in mind.

The principles and policies outlined in this document will be used in all laboratory operations, from project planning to data usage. This plan is to be followed by all staff of the Water Quality Laboratory in the performance of their duties.

The Quality Assurance Manual is reviewed annually and revised as needed by the Quality Assurance Officer. All laboratory personnel receive a numbered copy of the updated manual and sign a receipt sheet.

Specific procedures for individual analysis and tasks are described in their respective Standard Operating Procedures (SOPs).

3. Organization and Responsibilities

The laboratory is organized into three sections: Biology, Chemistry, and QA/QC, as shown on the organizational chart, page 3. The section heads, Senior Biologist, Senior Chemist, and Associate Chemist of QA/QC report to the Water Quality Superintendent.

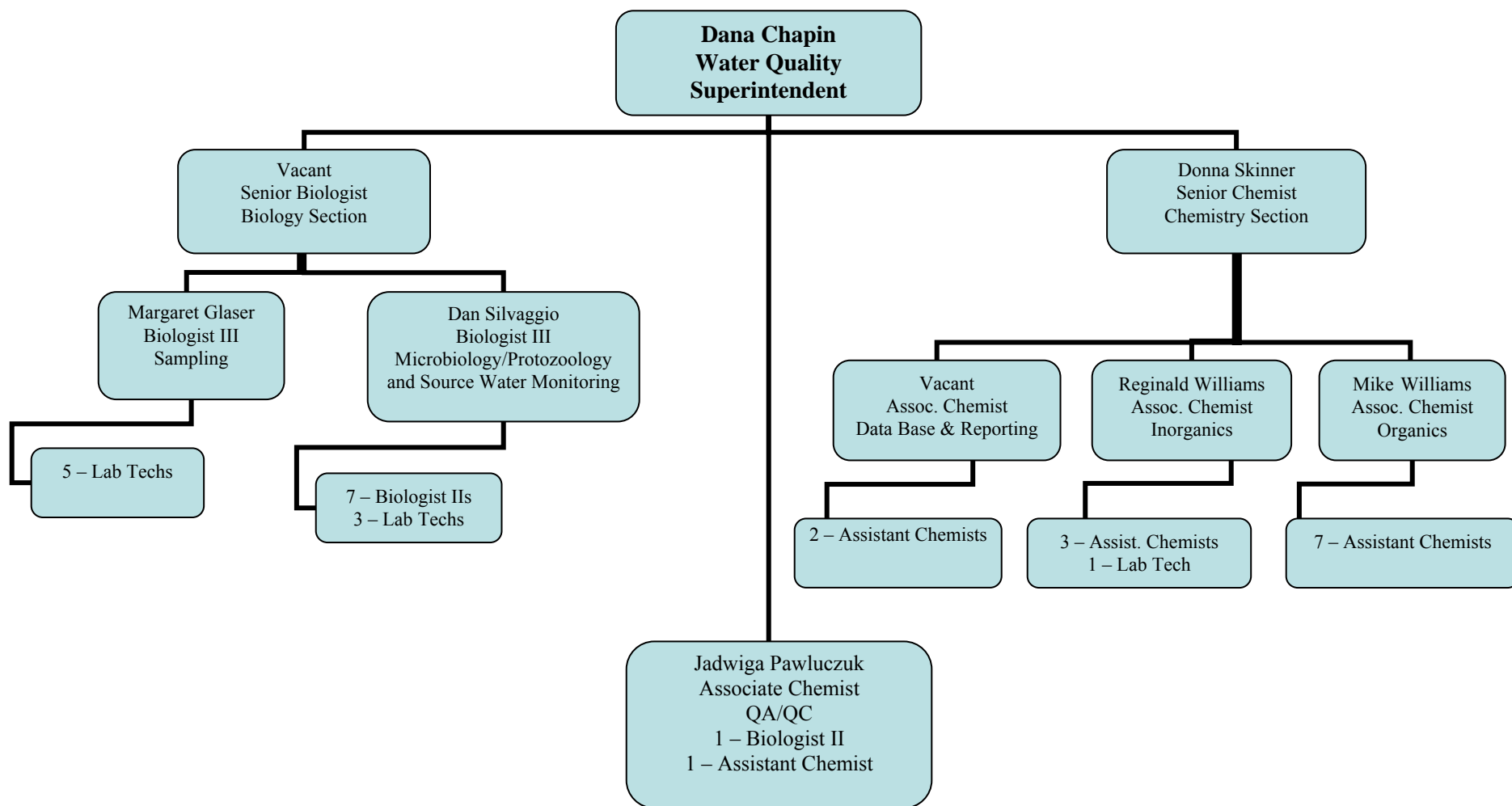
The Biology Section has two groups: Sampling, and Microbiology/Protozoology and Source Water Monitoring. All group supervisors (Biologists III) report to the Senior Biologist.

The Chemistry Section has three groups: Data Base and Reporting, Inorganics, and Organics. The supervisors (Associate Chemists) report to the Senior Chemist.

The Associate Chemist of the QA/QC section reports directly to the Water Quality Superintendent.

The City of San Diego Water Quality Laboratory Organization Structure

August 2007



Job Descriptions

All laboratory staff possess at least the minimum education and experience necessary for their positions, as specified by the City of San Diego Personnel Department.

Water Quality Superintendent is responsible for the overall operation of the laboratory. The Superintendent keeps current with proposed and enacted State and Federal regulations, monitors the current and future personnel and physical needs of the laboratory, and ensures that data is of high quality and produced in a timely manner. The Superintendent reports unusual events in the water system or any violations of drinking water standards to the California State Office of Drinking Water. The Superintendent is responsible for the development, implementation, and continued operation of the Quality Assurance Program.

Senior Chemist and Senior Biologist: coordinate and oversee the operation of the entire laboratory. They are responsible for ensuring that analyses are completed on time and are of required quality. They review current and proposed legislation for impact on the laboratory, review personnel and equipment requirements, and review and sign all external reports. They notify the Water Quality Superintendent of any unusual events or violations of mandated standards in the City of San Diego's water system. In coordination with the Quality Assurance Officer, they are responsible for overseeing the implementation and documentation of the Quality Assurance Program.

Quality Assurance Officer implements the WQL's Quality Assurance Program, reviews and approves quality control data, laboratory documentation and procedures, and the entire quality system. The Quality Assurance Officer (QAO) works closely with the Senior Biologist and Senior Chemist on the implementation of the Quality Assurance Program. The QAO and QA staff conduct internal audits of the laboratory, and report the results to the Laboratory Director. The QAO is responsible for storage and archiving of the laboratory data and documentation.

Associate Chemists and Biologists III (Group Supervisors) are first line supervisors with overall responsibility for all analysis and personnel issues within their groups. They are responsible for reviewing and approving all data, and keeping all procedures, the Quality Assurance program and results current. Associate Chemists and Biologists III ensure that all analytical work is performed safely and in accordance with SOPs and QA Manual. They schedule work assignments, ensure that all personnel receive training, and review future personnel and equipment needs.

Assistant Chemists and Biologists II are journey level analysts. They are responsible for performing a variety of analyses, ranging from simple to complex. They perform and troubleshoot all aspects of the assigned analysis without assistance. They review their data for correctness and quality. They review and update SOPs and other laboratory documentation. Assistant Chemists and Biologists II may train other analysts in laboratory procedures and instrument operation.

Junior Chemists and Biologists I are the entry level positions. They perform basic analyses with minimal assistance. They receive training and perform complex analyses under the tutelage of Assistant Chemists and Biologists II. They may advance to Assistant Chemists and Biologists II respectively, with a minimum of one year of environmental water laboratory experience and satisfactory performance.

Laboratory Technicians perform support tasks and less-complex analyses. The support tasks include, but are not limited to, field sampling; glassware preparation; and sample, media and reagent preparation. Laboratory technicians may assist the journey level analysts in chemical or biological analysis.

4. Quality Assurance Objectives for Data Measurement

The Quality Assurance Program for data measurement is designed to meet the following objectives:

- Document standard operating procedures (SOPs) for all procedures performed in the laboratory.
- Establish, implement, and monitor the necessary procedures to produce data of known quality.
- Maintain an ongoing assessment of the precision and accuracy of all laboratory data.
- Validate all data so it meets the precision and accuracy requirements for its intended use.
- Ensure corrective actions are followed and document when precision and accuracy requirements are not met.
- Verify the quality control system is operating within acceptable limits.
- Provide protocols for data validation.
- Ensure all data and documentation is legally defensible.
- Improve training of all analysts.
- Provide permanent records of instrument performance as a basis for data validation.
- Improve record keeping, storage and retrieval, and report writing.

5. Quality Assurance and Quality Control

Quality Assurance (QA) is a plan for laboratory operation that specifies the measures required to produce data of known and defensible quality.

Quality Control (QC) is a variety of measures and procedures that assure an analysis is “in-control”. An analysis is “in-control” when it is performed according to an approved method by properly trained personnel, with appropriate and standardized reagents, and adequately maintained and calibrated instruments.

5.1 Laboratory Housekeeping

The laboratory is maintained by City staff, building maintenance personnel, and contract custodial services. The laboratory staff is responsible for ensuring their work area is clean, uncluttered, and that all reagents, chemicals, solutions, and samples are labeled, stored, and disposed of according to Material Safety Data Sheets (MSDS), current regulations, SOPs, and Good Laboratory Practices (GLP) requirements.

All samples and testing materials, regarded as hazardous wastes, are disposed of in compliance with the current local, state, and federal regulations. Refer to the SOPs: *MISC-01 Waste Neutralization*, *MISC-04 Hazardous Waste Daily Collections* and *MISC-06 Hazardous Waste Storage and Removal*.

The bacteriology lab counters are disinfected daily and the floor is mopped and disinfected weekly. The chemistry lab benches are cleaned daily by the analysts and the floors are mopped weekly by the janitors.

Building temperature and air quality are maintained as constant as possible.

5.2 Personnel Training

The first line supervisors are responsible for determining training needs and requirements of analysts and staff under their supervision.

Initial analytical training for new staff is a priority. It is provided by experienced analysts and laboratory equipment vendors. The analysts must have completed training prior to performing any analysis unassisted. Continuing training opportunities are provided to ensure competence and maintenance of analytical skills. Continuing training includes attendance at conferences and seminars offered by the American Water Works Association (AWWA), the American Chemical Society (ACS), the American Society for Microbiology (ASM), Water Environment Federation (WEF), and other professional organizations or manufacturers.

Training on the laboratory procedures is documented by the trainers and supervisors on a Training Report form. The Quality Assurance section maintains all analytical training reports.

5.3 Laboratory Instrument and Equipment Maintenance

All analytical and building equipment is maintained, inspected and cleaned as specified in the SOPs or in the manufacturers' requirements.

The laboratory maintains service agreements with vendors for major instruments and equipment.

The WQL has all the analytical instruments necessary to perform every analysis for which it holds accreditation by the Environmental Laboratory Accreditation Program (ELAP). Routine maintenance of analytical instruments is performed by the analyst and is documented in designated logbooks. The section supervisor is responsible for ensuring the logbooks are current and accurate. Each instrument has a logbook. The logbook is kept with the equipment. The analytical instrument logbook documentation must include the following information:

- Date,
- Maintenance performed,
- Instrument or analysis problems,
- Corrective actions, when appropriate, and
- Analyst signature.

Major repairs and maintenance are performed by the instrument vendors. All defective instruments will be taken out of service until they have been repaired and shown to perform in accordance to method specific requirements.

5.4 Analytical Reagents, Standards, and Media

All chemicals, reagents and media meet SOP specifications. If not specified, only “Analytical Reagent Grade” (AR) or American Chemical Society (ACS) grade chemicals or better are used. Chemicals, reagents, and media are stored out of direct sunlight and refrigerated, if necessary, to prevent deterioration. Care is exercised to prevent cross-contamination. Flammable solvents are stored in a fire-proof, vented cabinet. Strong acids and bases are stored in separate cabinets. Oxidizing and reducing reagents are stored separately. Shelf life dates are closely monitored.

SOPs define reference materials required for a specific method. These reference standards are traceable to a national standard of measurement (i.e., NIST). Vendor concentration certificates indicate traceability to national standards of measurement and provide the measurement results and associated uncertainty of measurement.

All reference materials, reagents, and media are labeled with date received, date opened, analyst’s initials, and expiration date.

Logs are maintained for standards and media preparation, tracking lot used, date made, expiration date, dilutions, and preparer’s initials. Prepared reagents and standards are traceable to the original stock standard by a unique sample ID number and are clearly labeled with the contents, concentration, date prepared, expiration date, and preparer’s initials.

Outdated standards, reagents, and media are not used and are disposed of in compliance with all current local, state and federal regulations. Refer to the SOPs: *MISC-01 Waste Neutralization*, *MISC-04 Hazardous Waste Daily Collections* and *MISC-06 Hazardous Waste Storage and Removal*.

5.5 Reagent Water Quality

Reagent grade water for chemical and microbiological testing is produced by *Milli-Q®* and *NanoPure®* purification systems.

Reagent grade water for chemistry is checked via reagent blanks analyzed with every analysis, and by daily resistivity measurement. Purification system filters are changed when reagent blanks show consistent contamination traced to the specific system, or if the resistivity of reagent grade water falls below 17 Megohms.

Reagent grade water quality requirements for microbiological testing and monitoring frequency are described in SOP: PRP-05 *Reagent Water*. In addition, a bacteriological suitability test is performed any time a new system is installed or a new source of water used. Acceptable limits of water quality used in microbiology testing are listed in the 20th edition of *Standard Methods for the Examination of Water and Wastewater*, section 9020. All test results are kept in a centralized binder located in the microbiology laboratory (room # M10).

5.6 Labware Cleaning and Sample Container Preparation

Glassware is regularly washed with detergent, rinsed with tap water, rinsed with distilled water, allowed to dry, and stored in a designated area. Specific container preparation and sample preservation requirements are described in analytical SOPs.

Cleaning procedure (including the pH check for detergent residue and the inhibitory residue check) and sterilization procedure for non-disposable labware used in microbiological analysis are described in SOP: PRP-06: *Labware Cleaning and Sterilization*.

The pH check with bromothymol blue is performed weekly by the prep room staff. Results are kept in the Prep Room QA/QC log book (room # R30).

An inhibitory residue check is performed by the Biologists whenever a different brand of detergent is used or a labware washing method is changed. Results are kept in the QC notebook in the bacteriology lab (room # M10).

For additional information relating to labware cleaning procedure refer to the following SOPs: PRP-22 *AMSCO Reliance 470 Washer* and PRP-23: *AMSCO Reliance 475 Dryer*.

5.7 Sample Collection, Receiving, Storage, and Disposal

To ensure accurate laboratory data, all samples are collected and transported according to the 20th edition of the *Standard Methods for the Examination of Water and Wastewater*, sections 1060, 9060. Additional method-specific requirements are detailed in analytical SOPs. All samplers have received training in proper sampling techniques, procedures and protocols. Periodic refresher training is provided, if necessary.

5.7.1 Sample Collection

Distribution system samples are collected by samplers assigned to the Biology Section. Sampling protocols for microbiological and chemical samples are described in SOP: SAM-01 *Sampling*, and individual method SOPs.

Raw water reservoir samples and watershed samples are collected by the staff of the Source Water Monitoring group. Customer complaint, new main and main break samples are collected by Water Department personnel, who may be laboratory or non-laboratory staff.

All samples are assigned a unique laboratory log number (sample ID) by the Laboratory Information Management System (LIMS.) This log number, along with the sample location, date, and required analysis is printed on a sample label.

Samplers attach the appropriate sample label to the proper container, collect the sample, and then record the time, date, and other comments on the sampling route sheets. Field analyses are performed at this time, and recorded in field record sheets. Samples are transported to the laboratory within the required holding time; and in coolers containing cold packs to keep the samples within the required temperature range.

5.7.2 Sample Receiving and Storage

The sample receiving protocol is described in SOP: SAM-03 *Sample Receiving*. Upon return to the laboratory, the samplers transfer all samples to the designated sample receiving personnel. The sample receiving personnel physically inspect the samples, “receive” them in LIMS and sign and date the sampling sheets. The received samples are placed in storage or delivered to the appropriate analyst. Specific sample storage requirements are in analytical SOPs.

The sampler *first*-enters all field data into the LIMS. Entries are checked for accuracy through a *second* entry by another person.

Frequently, customer complaint and main break samples are delivered to the laboratory after normal working hours. These samples do not have pre-printed route sheets or labels. The sampler is responsible for logging the sample into the sample logbook, filling out a label and attaching it to the container, and placing the sample into the refrigerator located on the WQL's back loading dock. The following information will be entered into the sample logbook:

- Sampling date and time,
- Sample ID,
- Delivery date and time,
- SR (Service Request) or WAO (Work Assignment Order) number,
- Sample location and comments, and
- Sample type.

The microbiology personnel receive these samples, log them into the LIMS and generate LIMS labels.

Signed and dated sample route sheets, covering the last 3 months, along with field data sheets are kept in the Database Section office. Older records are archived.

5.7.3 Chain of Custody

Chain of custody for samples collected by WQL personnel is documented on sampling sheets. Refer to the SOP: *SAM-03 Sample Receiving*.

5.7.4 Sample Disposal

Water samples for chemical analyses are disposed of only after all analyses have been completed, the data reviewed by the analyst's supervisor, and the results reports are released. The non-acidified water samples are not hazardous waste and are flushed down the laboratory sinks. All samples and testing materials regarded as hazardous wastes are disposed of in compliance with all current local, state and federal regulations.

Acidified samples are neutralized in acid neutralization tanks and flushed down designated sinks. Chemical hazardous waste is stored in a locked vented shed and hauled by a licensed contractor. Refer to the SOPs: *MISC-01 Waste Neutralization*, *MISC-04 Hazardous Waste Daily Collections* and *MISC-06 Hazardous Waste Storage and Removal*.

5.8 Analytical Instruments and Equipment Calibration

All measurement and test equipment necessary to support laboratory operations is calibrated and/or verified prior to being placed into service, and as scheduled or required thereafter. This includes, but is not limited to, analytical instruments, balances, ovens, refrigerators, freezers, incubators, water baths, temperature measuring devices, sample preparation devices, and volumetric dispensing devices. Calibration and calibration verification procedures for analytical instruments and other equipment are described in analytical SOPs.

The following elements of instrument calibration and calibration verification are essential, and adhered to by WQL staff:

- Details of initial instrument calibration procedures and acceptance criteria are specified in the method SOP.
- All raw data, calculations and interpretations of calibrations are documented and retained.
- Initial calibrations must be verified with a standard obtained from a second source (different vendor) and traceable to NIST.
- When an initial instrument calibration is not performed on the day of analysis, the validity of the initial calibration is verified prior to sample analyses by a batch calibration verification check (called often in EPA reference methods as “Continuous Calibration Check”) in each batch run. Sample results are quantified from the initial instrument calibration and not from any calibration verification check. If calibration verification check results are outside established acceptance criteria, corrective actions must be performed including repeating instrument calibration procedure.

Batch analytical instrument calibration documentation is kept with raw data.

Documentation for other laboratory equipment is kept in the Quality Assurance office (room # J18).

5.9 Standard Operating Procedures and Laboratory Forms

- 5.9.1 All analytical methods and general procedures used in the laboratory require a detailed SOP. Each analysis and procedure is performed according to its SOP. The Quality Assurance section maintains all original SOPs. SOPs are reviewed and amended whenever there are changes in methods or laboratory equipment. All SOPs will be approved by the Senior Biologist or Senior Chemist, Quality Assurance Officer and a first line Supervisor prior to use.
- 5.9.2 All SOPs are stored on the laboratory computer shared “J” drive in designated file folders.

- 5.9.3 All SOPs are written according to guidelines provided in the SOP: *GEN-09 Preparation of the SOPs*, located in the folder:
<J:\\WTRLims\\Quality Assurance\\SOPs\\CURRENT\\Quality Control>
- 5.9.4 The laboratory forms are controlled, as described in the SOP: *GEN-10 Document Control*.
- 5.9.5 All current SOPs are stored in the folder:
<J:\\WTRLims\\Quality Assurance\\SOPs\\CURRENT>
- 5.9.6 All current forms are stored in the folder:
<J:\\WTRLims\\Quality Assurance\\Forms>

5.10 Modification of Analytical SOPs

The criteria for modifying procedures are

- Compliance with the most recent approved revision of the reference method,
- Change in instrumentation,
- Improved data quality,
- Decreased analytical cost,
- Increased efficiency, and
- Ease of analysis.

Modifications of analytical SOPs are made according to the procedure outlined in the SOP: *GEN-10 Document Control* SOP. The SOP is located in the folder:
<J:\\WTRLims\\Quality Assurance\\SOPs\\CURRENT\\Quality Control>

No procedural change may be initiated without prior modification of a Standard Operating Procedure.

5.11 Method Detection Limits

The Method Detection Limit (MDL) is defined in the Federal Register (40 CFR Part 136, Appendix B) as “*the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte’s concentration is greater than zero*”. Specific MDL information, requirements, and frequency of verification are described in analytical SOPs.

MDLs are determined by analyzing at least seven replicates of a sample containing the analyte of interest at a concentration ranging from one to five times the estimated method detection limit. The replicates are analyzed over a period of three or more days to ensure the MDL determination is more representative. The MDL is then calculated as described in the *40 CFR 136*. A copy of the *40CFR 136* can be obtained from the QAO.

The analysts prepare MDL reports for all MDL determinations. All MDL data are reviewed and approved by the group's supervisor, the Senior Chemist, and the Quality Assurance Officer before taking effect. The Quality Assurance Section updates the LIMS and maintains the original MDL Reports.

Laboratory MDLs must be at or below the Title 22 Detection Limits for Reporting (DLR).

MDLs are verified annually or as otherwise stated in the method SOP, or any time when

- A new instrument is being placed into service,
- A new method is being developed,
- A new analyst is being trained, or
- A major change is made to the instrument (such as installing a new column).

5.12 Quality Control Checks

Required quality control check samples and acceptance criteria are described in analytical method SOPs.

5.12.1 General Terminology

The following list of terms refers to different types of QC used in the laboratory.

A. Positive/Negative Controls:

Total Coliform(-)/Fecal Coliform(-):	<i>Pseudomonas aeruginosa</i>
Total Coliform(+)/Fecal Coliform(-):	<i>Klebsiella pneumonia</i> or <i>Enterobacter aerogenes</i>
Total Coliform(+)/Fecal Coliform(+):	<i>Escherichia coli</i>
Enterococcus(+) control:	<i>Enterococcus faecalis</i>
Enterococcus(-)control:	<i>Escherichia coli</i>

B. Laboratory Reagent Blank (LRB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, reagents and sample preparation procedures (such as extraction, digestion, or filtration) to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

- C. Field Reagent Blank (FRB):** An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and is treated as a sample in all respects (see definition for LRB) including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.
- D. Field Duplicates:** Two separate samples collected at the same time from the same sample site, placed under identical circumstances and treated exactly the same throughout field and lab procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with lab procedures.
- E. Laboratory Duplicate/Microbiology:** Two aliquots of the original sample, split in the laboratory, analyzed with identical procedures and within the same analytical run, but analyzed by different analysts. This is to provide a measure of intra-analyst precision.
- F. Laboratory Duplicates (LD):** Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- G. Laboratory Fortified Sample Matrix (LFM) (spiked sample):** An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is processed and analyzed exactly as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot.
- H. Laboratory Fortified Blank (LFB), (spiked reagent water):** An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly as a sample to determine whether the method is in control and whether the laboratory is capable of making accurate and precise measurements.
- I. External Check Samples or Quality Control Samples (QCS):** A solution of method analytes of known concentrations prepared from a source different from the source of calibration standards. It is used to check either laboratory or instrument performance.

- J. Internal Standard:** A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.
- K. Surrogate Analyte:** A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.
- L. Continuous Calibration Check (CCC):** One of the calibration standards analyzed throughout an analytical run to verify the previously established calibration curve and accuracy of quantitation.
- M. Lab Performance Check Solution (LPC) or Instrument Performance Check Solution (IPC):** A solution of method analytes, surrogate compounds, and internal standards (usually a mid-range calibration standard) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.
- N. Tuning Solution:** A solution used to determine acceptable instrument performance prior to calibration and sample analysis.
- O. Linear Dynamic Range (LDR):** The concentration range over which the instrument response to an analyte is linear.

5.12.2 QC Calculations

Two QC measures used daily on most analytical determinations are precision, calculated from the results of duplicate or replicate analysis, and accuracy calculated from the results of spiked samples, external QC checks, fortified blanks, and other checks specified in SOPs. Precision is expressed as % RPD (Relative Percent Difference) or % RSD (Relative Standard Deviation). Accuracy is expressed as % Recovery.

Sample Mathematical Calculations

- A. Arithmetic average (mean) \bar{X} of a sample and its duplicate:

$$\bar{X} = \sum x_i / n$$

$\sum x_i$ = sum of the measurements

n = number of measurements

- B. % RPD is used for sample and its duplicate:

$$\%RPD = [(A-B)/\bar{X}] * 100\%$$

Example: sample (A) = 201 mg/L, duplicate (B) = 193 mg/L, mean (\bar{X}) = 197 mg/L. The calculated %RPD is 4.06%.

- C. % RSD is used for three or more replicates:

$$\%RSD = s/\bar{X} * 100\%$$

s = estimated sample standard deviation

Example: sample = 201 mg/L, replicate 1 = 193 mg/L, replicate 2 = 214 mg/L; Mean = 203 mg/L. The calculated estimated sample standard deviation, s = 8.65

$$\%RSD = (8.654/203) * 100\% = 4.26\%$$

- D. LFB and QCS %Recovery = $x_i/x_t * 100\%$

x_i = measured value

x_t = true value

- E. % Recovery of Matrix Spike:

$$\frac{(\text{conc. of spiked sample} - \text{conc. of sample w/o spike}) * 100\%}{\text{conc. of added spike}}$$

Example: 100 ml of an unspiked sample measuring 9.50 mg/L was spiked with 100 μ L of a 5000 mg/L standard (5.00 mg/L spike), and this spike sample measured 13.7 mg/L.

$$\%Recovery = \frac{(13.7 - 9.50)100}{5.00} = 84.0\%$$

- F. Calculation of arithmetic average and matrix spike recovery when one of sample replicates is below method detection limit (MDL) and reported as ND.

Example: sample and sample replicate were measured as 6.74 mg/L and 4.85mg/L. The sample was spiked with 25.0 mg/L. Spiked sample measured 29.2 mg/L.

The analyte's MDL is 5.0 mg/L. Consequently, value of 4.85 mg/L was reported as ND.

For the calculation of average and spike recovery consider ND as "0."
Using formula in "A" above, arithmetic average is:

$$X = (0+6.74)/2 = 3.37 \text{ mg/L} = \text{ND}$$

Spike recovery then, using formula in "E" above is:

$$\% \text{ Rec.} = \frac{(29.2 - 0) * 100}{25.0} = 117\%$$

5.13 Data Acquisition and Reduction

- 5.13.1 Most of the instruments in the WQL process data automatically. For tests which do not have automatic data reduction, the raw data is recorded on analytical batch LIMS sheets.
- 5.13.2 All notations on data printouts and sheets will be in indelible black or blue ink. Correction fluid of any type, pencils, and pens with "erasable ink" will not be used.
- 5.13.3 Corrections are made by lining-through so that the original entry is legible and entering the correction directly above it. Changes need to be initialed and dated, and the reason for change noted.
- 5.13.4 If reported values are "corrected", all corrections must be explained and equations used to derive final "corrected" results noted on data sheets and printouts.
- 5.13.5 Instrument maintenance, unusual events, and corrective actions relating to the instrument and method performance are recorded in the instrument logbook. Each entry must be written in indelible black or blue ink, and signed and dated.
- 5.13.6 The printouts and analysis logbooks are stored in a safe and orderly manner.
- 5.13.7 All analyses are completed according to the current SOPs.

5.14 Data Review, Documentation, Entry, and Validation

- 5.14.1 All data, as run in an analytical batch, (whether within the QC acceptance limits or not), is entered into the LIMS within the time limit specified in the method SOP. Data not meeting all QC requirements will be entered as "N" (non-reportable) in LIMS.**
- 5.14.2 The analyst has primary responsibility for verifying that all QC parameters and checks are within the acceptance limits before entering data and submitting it to the supervisor for review. Review at the analyst's level enables most errors to be caught immediately and prevents delays in reporting data.
- 5.14.3 All data is validated through a multi-step review process. The process is designed to ensure that the data is of a known quality. It is as follows:
- A. The analyst ensures that the following are clearly identified:
 - Date and time stamp from instrument printouts representing the true date and time;
 - The analyst name; and
 - The concentration units.
 - B. The analyst reviews raw data for completeness and adherence to QC standards.
 - C. The analyst documents data by noting the following information on the raw data sheets:
 - True values and acceptance range for all QC checks (in concentration units);
 - Dilution factors (if not printed);
 - Reasons and explanations for any non-reportable ("N") values; and
 - Other comments which may help in data interpretation, verification; and reconstruction. (For example, if reported values are corrected, all corrections must be explained.)
- Data documentation may be supplemented by attaching a LIMS *Quality Control Performance Summary Report*.
- D. Data documentation must include information which would allow the auditor to reconstruct the final results.

- E. The analyst signs and dates the first page of raw data.
- F. Data is then entered into LIMS manually or via electronic transfer.

Manual data entry, first and second, must be done from original raw data. Raw data is a printout from an automated system, or a value handwritten on a batch sheet where there is no automatically printed analytical record.

Examples: A batch printout from IC, GC-MS, AA, turbidity meter, auto-titrator; likewise handwritten on LIMS batch sheets microbiological, TON, and total hardness data.

Manual data entry is as follows:

- The analyst enters values, acceptance ranges for QC checks and spikes, explanations for any “N” (non-reportable) data, and any other comments pertaining to data interpretation and validation, in the *first entry* of the *Results Center* of LIMS.
- Data is then *second entered* by another person (it may not be done by the analyst who produced that data.) **The purpose of the second entry is to verify accuracy of the first entry and to correct any discrepancies.**

Electronic data transfer (replaces *first* and *second* manual entry) allows for direct download of data and comments into LIMS.

Electronic data transfer is as follows:

- The analyst creates an ASCII text file using LimsLink software. The file contains batch data.
 - The analyst transfers the data file into LIMS; then enters appropriate comments with acceptance ranges for QC checks and spikes, and explanations for any “N” (non-reportable) data.
 - To mark a value as non-reportable (“N”), the analyst must access data in LIMS.
- G. The supervisors review data, documentation, and data entry for correctness. The supervisors are responsible for ensuring that the data meets the method specific QC requirements.
 - H. The final review and “release” of data in LIMS is performed by the designated laboratory staff in the QA and data base sections. “Release” of data makes it available for reporting.

5.15 Data Reporting

The State of California Department of Health Services requires chemical data to be reported to three significant figures and microbiological data to two significant figures. Data not reported to the State may be reported in fewer significant figures, if specified in SOP.

For more information about significant figures, refer to the section 1050B of the 20th edition of the *Standard Methods*.

5.15.1 Rounding Data

Round off data using the rules below. These rules follow rounding off convention used by most of computer applications.

- A. When the digit immediately after the one to be retained is less than 5, that digit is dropped and the retained digit is kept unchanged.
Example: 2.4549 rounded to 3 significant figures become 2.45.
- B. When the digit immediately after the one to be retained is 5 or more, that digit is dropped and the retained digit is increased by one.
Example: 2.4554 rounded to 3 significant figures become 2.46.
- C. When performing a complex calculation, such as standard deviation, carry several extra figures through the computation and then round off the final answer to the proper number of significant figures.

5.15.2 Significant Figures

Data needs to be reported with the number of digits justified by its accuracy and precision. That is, reported data needs to be rounded off to the number of digits consistent with the confidence that can be placed in them. The State of California Department of Health Services requires chemical data to be reported to three significant figures and microbiological data to two significant figures.

Statistical computations need to precede any rounding off that is performed on the data reported. For example, the average of replicates needs to be calculated with at least one more figure than the required number of significant figures for that analysis. For reporting purposes, the average will then be rounded off to the proper number of significant figures.

5.15.3 Zero

The number zero may or may not be a significant figure depending on the situation.

Final zeros after a decimal point are always meant to be significant figures.

Example: To the nearest milligram, 9.8 g is reported as 9.800 g.

In counting significant figures, any zeros used to locate a decimal point are not considered significant.

Example: 0.00251 contains only 3 significant figures, and 0.002 contains only 1 significant figure.

Zeros are not be added to the right of significant figures to define the magnitude of a value unless they are significant, since they would confuse the significance of the value.

Example: It is not a good practice to report a value as 2510 mg/L. If the data is reliable to only 3 significant figures, it is clearer to report the value as 2.51 g/L or 2.51×10^3 mg/L, either of which clearly expresses 3 significant figures.

However, our specified reporting units of measure may require us to report values with zeros which have ambiguous significance.

Example: 1020 mg/L may have 3 or 4 significant figures, which can be clarified as follows:

- To indicate 4 significant figures, place a decimal point to the right of the last zero, 1020. mg/L, or
- To indicate 3 significant figures, either
 - Use exponential notation, 1.02×10^3 mg/L; or
 - Use higher units of measure, 1.02 g/L.

5.15.4 Significant Figures in Calculations

A. In multiplication and division, the operator with the least number of significant figures determines the number of significant figures to be reported in the calculated result.

Example: The product of $1256 \mu\text{g/L} \times 12.2 = 15323.2 \mu\text{g/L}$ is to be reported as 15.3 mg/L.

- B. In addition and subtraction, the least number of figures to the right of the decimal point determines the number of figures to be reported in the result.

Example: The sum of $120.05 + 10.1 + 56.323 = 186.473$ is to be reported as 186.5, because value 10.1 with the smallest number of decimal places defines the reporting level.

- C. In mixed calculations involving multiplications and subtractions, for example, the operation is done serially, and the final result is rounded according to the least number of significant figures involved.

Example: $(1256 \mu\text{g/L} \times 12.2) - 125 \mu\text{g/L} = 1.53 \times 10^4 \mu\text{g/L} - 125 \mu\text{g/L} = 1.52 \times 10^4 \mu\text{g/L}$ or 15.2 mg/L.

5.16 Corrective Actions

Corrective action is required whenever a method or instrument performance fails to meet established criteria and acceptance limits.

Corrective action begins with the analyst, who is responsible for knowing when the analytical process is out-of-control. Out-of-control events include QC outliers, hold-time failures, loss of sample, equipment malfunctions, and evidence of sample contamination. All out-of-control events are reported to the supervisor. The first line supervisor reviews the corrective actions taken and ensures the analysis is brought into control. The appropriate corrective actions are outlined in the SOPs. Possible corrective actions are also outlined in the section 1020 B.14 of the 20th edition of the *Standards Methods*. The goal of corrective action(s) is to

- Obtain data of acceptable QC,
- Identify problems with methods or techniques and minimize their recurrence, and
- Develop a historical record detailing the problem and its resolution.

A recurring out-of-control condition indicates a problem with the analysis. The problem may be due to instrumentation, deviation from SOP, analyst error, or other method problem. When a recurring out-of-control condition is found, the first line supervisor investigates the problem and takes all actions necessary to correct the situation.

All analytical problems and corrective actions taken are documented in the analysis/instrument logbook and on raw data sheets. All notations on raw data must be referenced in the logbook. Corrective action documentation includes:

- A description of the problem,
- The implementation of corrective action, and
- A demonstration that corrective action has been effective.

5.17 Record Keeping

Records of samples, sample testing, and results are entered into LIMS. All information recorded throughout the testing process is retrievable. Backup copies of LIMS data are kept to prevent loss due to computer failure.

All records of chemical analyses of compliance samples are retained for at least ten (10) years (40 CFR 141.33). If the analysis is for lead or copper, then the records are retained for an additional two (2) years for a total of twelve (12) years (40 CFR 141.91). All microbiological compliance testing records are retained for at least five (5) years (40 CFR 141.33).

These records include

- All raw data of sampling and analyses;
- Calculations, notes, and observations;
- Final reports;
- SOPs;
- Instrument and analysis logbooks;
- All correspondence relating to laboratory activities;
- All corrective action reports, audits, and audit responses;
- Proficiency test results; and
- Personnel records.

Records for the current and previous year are kept in the laboratory. All prior records are archived. Detailed procedures for data retention and archiving are described in the SOP: *QA-03 Quality Assurance Record Retention/Archives*, located in the folder:

<J:\WTRLims\Quality Assurance\SOPs\CURRENT\Quality Control>

5.18 Computers and Electronic Data

The WQL utilizes an electronic data system (LIMS) for record keeping. Policies and procedures that ensure the integrity of data through entry, storage, transmission, processing and reporting are in effect.

The lab data system is maintained and serviced by an in-house data group, as well as the San Diego Data Processing Corporation. This practice ensures that the system functions properly and is reliable.

Data security is maintained through the use of passwords and by restricting the use of certain functions to authorized persons. In addition, results are protected from unauthorized amendment by locking the records once they are released for reporting.

5.19 Subcontracting of Testing

All contract laboratories used for testing samples for the WQL are fully accredited by ELAP for the analyses they are contracted to perform.

The contract laboratory must use EPA approved testing methods, and follow all QA and QC requirements, unless deviations are agreed upon and approved by the WQL in advance.

5.20 Quality Assessment

Quality Assessment is a process used to ensure that quality control measures are performed as required, and to determine the quality of data produced by the WQL. Quality assessment includes internal blind checks, external proficiency testing study, raw data audits, internal quality system audits, and external quality system audits.

5.20.1 Internal Blind Checks

Internal Blind Checks are provided by the Quality Assurance Section. They are issued upon request from any supervisor for training purposes, internal check purposes, or comparison study with Proficiency Testing (PT) samples. Analysts are expected to achieve a recovery within the SOPs established acceptance range.

5.20.2 External Proficiency Testing (PT) Study

The WQL is required by ELAP to participate in proficiency testing (PT) studies prior to the granting of certification and annually thereafter. The WQL must successfully analyze PT samples for all parameters and matrices for which it is certified and for which PT samples are available.

5.20.3 Raw Data Audits

Raw data audits are conducted to assess adherence to standard operating procedure and data documentation requirements. They are conducted internally by the Quality Assurance Section using a random sample of data. The goal is to detect any deviations from the SOP and data documentation protocol described in section 5.12 of this manual.

5.20.4 Internal Quality System Audits

The Quality Assurance Section staff conducts internal quality system audits to verify that laboratory operations continue to comply with the requirements of the QA plan as outlined in this Manual. Internal audits are used for self-evaluation and improvements.

The auditor notifies the Water Production Superintendent, Senior Chemist and Senior Biologist in writing, about any discrepancies and recommends corrective actions.

5.20.5 External Quality Systems Audits

External system audits are conducted by auditors of the State of California Department of Health Services Environmental Laboratory Accreditation Program (ELAP). These audits are part of the renewal of the laboratory's accreditation. Deficiencies noted in the audit are corrected and documented in an official response to ELAP within the required time frame.

6. References

- 6.1 EPA 815-B-97-001 Manual for the Certification of Laboratories Analyzing Drinking Water, Criteria and Procedures-Quality Assurance, 5th Edition, January 2005.
- 6.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998
- 6.3 Taylor, J.K., Quality Assurance of Chemical Measurements, Lewis Publishers, Inc., 1987.
- 6.4 CFR 40, 136
- 6.5 CFR 40, 141
- 6.6 CCR, Title 22