

Overview of Quality Assurance Project Plans

Prepared for the County of
San Diego Dry Weather
Monitoring Workgroup

3/15/06



DQOs – Data Quality Objectives

- Needed to have comparable data.
- Meet project objectives (e.g. Basin Plan, CDFG, Multi-sector permit, TMDLs).
- Evaluate trends
- Decision making
- Legally Defensible

From Last Year's DWMWG Meeting

Data quality is defined by a series of statements that set standards the data must meet. These standards cover the way the sample is collected and analyzed. In general, certain performance criteria (data quality objectives) are established to ensure that the data are acceptable and usable. The data quality assurance and control (DQAC) process is a strategic planning approach based on scientific methods to prepare for data collection activities. It provides a systematic procedure for defining the criteria that a data collection design should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision error for the study, and how many samples to collect, balancing risk and cost in an acceptable manner. **Using the DQAC process will assure that the type, quantity, and quality of environmental data used in decision making will be appropriate for the intended application, resulting in environmental decisions that are technically and scientifically sound and legally defensible.**

Source: http://www.projectcleanwater.org/summaries/02-16-05_monitoring_dry_wg_summary.pdf.

Table 3-1
Data Evaluation
(Note 1)

QC Element (Sample Type, Analysis Condition, or Characteristic)	Type of Failure	Possible Causes (Note 2)	Major PARCCS Parameters Affected (Note 3)	Possible Effect on Data (Documented in CQAR)	Worst Case Data Evaluation (Documented in CDQAR) (Note 4)
Chain of custody	Chain broken or not kept	<i>Missing signatures; missing seals; missing dates/times.</i>	Completeness	Incomplete data	Data not legally defensible.
Sample labeling	Sample labels unreadable, missing or not attached to containers	<i>Failure to protect from moisture; failure to use appropriate marker or labels; improper SOP</i>	Representativeness Completeness	Incomplete data False positives False negatives	Invalidates all sample results.
Sample labeling	Samples mislabeled	<i>Sampler error; improper SOP.</i>	Representativeness	Incomplete data False positives False negatives	Invalidates all sample results.
Sample containers	Plastic container for organic analytes	<i>Samplers unaware of requirement; improper SOP; failure to read SAP; SAP incorrect; insufficient containers.</i>	Representativeness Accuracy Completeness	False positives False negatives High or low bias Phthalate interference	Invalidates all sample results.
Sample containers	Glass containers for boron, silica, & fluoride	<i>Samplers unaware of requirement; improper SOP; failure to read SAP; SAP incorrect; insufficient containers.</i>	Representativeness Accuracy Completeness	False positives High bias	Invalidates all sample results.
Headspace	Bubbles in water VOC vial > 6 mm; visible headspace in soil VOC container.	<i>Poor sampling technique; caps not sealed tight; septum caps not used; dirt between cap and rim; soil not packed tight; improper SOP</i>	Representativeness Accuracy Completeness	False negatives Low bias	Invalidates all sample results. Sample results > DL considered as minimum values only.

Source: www.usace.army.mil/usace-docs/eng-manuals/em200-1-6/c-3.pdf

Have a Written QA Plan!!!!

Why?

- Required in new permit.
- Field staff know the expectations.
- Managers have confidence that resources are not being wasted.
- Decision Matrix (Follow ups, IC/ID)
- Program becomes effective and useable.

QAPP Development

SWAMP QAPP

- <http://www.swrcb.ca.gov/swamp/qamp.html>

Key components of a QAPP

- Program overview
- Org Chart
- Sample Location Map
- List of sampling and analytical methods
- List of sample equipment/meters
- List of sample containers, preservatives, holding times
- Detection limits and reporting limits
- Field Logs
- Calibration Requirements, frequency, and logs
- Sample handling procedures
- QA Field Samples-Level is often dictated by sensitivity and budget
 - Blanks (equipment rinse, field, trip blanks for VOCs)
 - Known (certified) standards
 - Duplicates
 - Splits

Key components (cont.)

- Specify Laboratory
- Establish project specific laboratory QC requirements:
 - Specified methods and detection limits
 - What defines a batch?
 - Method blank
 - Duplicates
 - QCS/LCS
 - Matrix spikes
 - Report Format/EDDs

Table 6. Summary of Sample Container, Volume, Initial Preservation, and Holding Time Recommendations for Water Samples

Parameters for Analysis in WATER Samples	Recommended Containers (all containers pre-cleaned)	Typical Sample Volume (ml)	Initial Field Preservation	Maximum Holding Time (analysis must start by end of max)
Conventional Constituents in Water				
Alkalinity	Polyethylene bottles (see NOTE ¹⁾ below)	100 ml	Cool to 4°C, dark	14 days at 4°C, dark
Chloride (Cl), Sulfate (SO ₄) and Fluoride (F)	Polyethylene bottles (see NOTE ¹⁾ below)	300 ml	Cool to 4°C, dark	28 days at 4°C, dark
Ortho-phosphate (OPO ₄)	Polyethylene bottles (see NOTE ¹⁾ below)	150 ml	Cool to 4°C, dark	48 hours at 4°C, dark
Nitrate + Nitrite (NO ₃ + NO ₂)	Polyethylene bottles (see NOTE ¹⁾ below)	150 ml	Cool to 4°C, dark	48 hours at 4°C, dark
Total Kjeldahl Nitrogen (TKN)	Polyethylene bottles (see NOTE ¹⁾ below)	600 ml	Cool to 4°C, dark	Recommend: 7 days Maximum: 28 days Either one at 4°C, dark
Total Dissolved Solids (TDS)	Polyethylene bottles (see NOTE ¹⁾ below)	1000 ml	Cool to 4°C, dark	7 days at 4°C, dark
Ammonia (NH ₃)	Polyethylene bottles (see NOTE ¹⁾ below)	500 ml	Cool to 4°C, dark	48 hours at 4°C dark; if acidify, 28 days at 4°C, dark
Total Phosphorus (TPO ₄)	Polyethylene bottles (see NOTE ¹⁾ below)	300 ml	Cool to 4°C, dark	28 days at 4°C, dark
NOTE: The volume of water necessary to collect in order to analyze for the above constituents is typically combined in four 1-liter polyethylene bottles, which also allows enough volume for possible re-analysis and for conducting lab spike duplicates. This is possible since the same laboratory is conducting all of the above analyses; otherwise, individual volumes apply.				
Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC)	40 ml glass vial	40 ml (one vial)	Cool to 4°C, dark	28 days at 4°C, dark
Total Suspended Solids (TSS)	500 ml amber glass jar	1000 ml (two jars)	Cool to 4°C, dark	7 days at 4°C, dark
Suspended Sediment Concentration (SSC)	500 ml amber glass jar	500 ml (one jar)	Cool to 4°C, dark	7 days at 4°C, dark
Chlorophyll a Pheophytin a	1-L amber polyethylene bottle	1000 ml (one bottle)	Cool to 4°C, dark	Keep at 4°C, dark, but must filter within 48 hours. Filters may be stored frozen up to 30 days.

Data Acceptability Criteria for Conventional Constituents in Water				
Sample Type	Objective	Frequency of Analysis	Recommended Control Limits	Recommended Corrective Action
External Calibration Calibration Standards (3-5 standards over the expected range of sample target analyte conc., with the lowest conc. Sto at or near the MDL).	Full calibration: Establish relationship between instrument response and target analyte conc.	Follow manufacturer's or procedures in specific analytical protocols. A min. 5 point calib. Each set up, major disturbance, and when routine calib check exceeds specific control limits.	Linear regression, r>0.995	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Calibration Verification Calibration Check Standards (minimum of one mid-range standard prepared independently from initial calibration standards).	Verify calibration.	After initial calibration or recalibration. Every 20 samples.	%Recovery = 80 -120%	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Method Detection Limit Determination (MDL) Spiked matrix samples (analyte-free water samples to which known amounts of target analytes have been added; one spike for each target analyte at 3-10 times the estimated MDL).	Establish or confirm MDL for analyte of interest.	Seven replicate analyses prior to use of method. Re-evaluation of MDL annually.	Determined by program manager.	Redetermine MDL.
Accuracy and Precision Assessment Reference materials (SRMs or CRMs, covering the range of expected target analyte conc).	Assess method performance (initial method validation and routine accuracy assessment).	Method validation: As many as required to assess accuracy and precision of method before routine analysis of samples. Routine accuracy assessment; one (preferably blind) per 20 samples or one batch.	Measured value <95% confidence intervals, if verified. Otherwise, %Recovery = 80-120%	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Matrix spikes (field water samples to which known amounts of target analytes have been added; 5 times the concentration of analyte of interest or 10 times MDL).	Assess matrix effects and accuracy (%R) routinely.	One per 20 samples or one per batch, whichever is more frequent.	%Recovery = 80-120% or Control Limits based on 3x the standard deviation of laboratory's actual method recoveries.	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data. Zero percent recovery requires rejection of all suspect data.
Matrix spike replicates (replicate aliquots of matrix spike samples; 5 times the concentration of analyte of interest or 10 times MDL).	Assess method precision routinely.	One duplicate per 20 samples or one per batch, whichever is more frequent.	RPD <25% for duplicates.	Determine cause, take appropriate corrective action. Recalibrate & reanalyze all suspect samples or flag all suspect data.
Laboratory Duplicate	Assess method precision	One per 20 samples or one per batch, whichever is more frequent.	RPD <25% for duplicates.	Determine cause, take appropriate corrective action. Recalibrate & reanalyze all suspect samples or flag all suspect data.
Field Replicate (replicate aliquots of water field samples).	Assess method precision routinely. Assess total variability (i.e., population variability, field or sampling variability, & analytical method variability.)	1% annual rate (5% of total number of field samples per analytical procedure per year; rounded up to nearest whole number).	RPD <25% for duplicates.	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.

Precision

Laboratory Replicates for Precision

A minimum of one field sample per batch of SWAMP samples submitted to the laboratory will be processed and analyzed in duplicate or more for precision. The relative percent difference among replicate samples (RPD expressed as percent) will be less than the DQO's listed in Appendix C for each analyte of interest. Following are the calculations:

Each measured value is compared against the known value of the standard, and accuracy is expressed as the relative percent difference.

$$RPD = \frac{[V_m - V_k]}{V_k} \times 100\%$$

Where: RPD = the relative percent difference

V_m = the measured value,

V_k = the known value.

Accuracy

Recovery is the accuracy of an analytical test measured against a known analyte addition to a sample. Recovery is calculated as follows:

$$\text{Recovery} = \frac{(\text{Matrix plus spike result} - \text{Matrix result}) \times 100}{\text{Expected matrix plus spike result}}$$

Completeness

Completeness is defined as “a measure of the amount of data collected from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement” (Stanley and Verner, 1985). Field personnel will always strive to achieve or exceed the SWAMP completeness goals of 90% (85% for fish, clam, and mussel tissues) for water, sediment, or biota (biological assessment) samples.

County of San Diego Dry Weather Program

- Many of the elements of a QA plan are done.
- List of Parameters, Methods and Detection Limits.
- List of DQOs (limited to dry weather methods and action level). What about others???
- Standardized Field Data Sheets.
- Regional Data Sharing Format.

Dry Weather Analytes and RLs

2005 Reporting Limits for Laboratory Analytes*

Analyte	Reporting Limit	Unit
Oil and Grease	5	mg/L
MBAS	0.5	mg/L
Diazinon	0.05	µg/L
Chlorpyrifos	0.05	µg/L
Cadmium	5	µg/L
Copper	5	µg/L
Lead	5	µg/L
Zinc	20	µg/L
Total coliform	20 (Quantify up to 1,600,000)	MPN/100 mL
Fecal coliform	20 (Quantify up to 160,000)	MPN/100 mL
Enterococcus	20 (Quantify up to 160,000)	MPN/100 mL

*Adopted by the Dry Weather Monitoring Workgroup on April 13, 2005

2005 Action Levels for Field Screening and Laboratory Analytical Parameters

Field Screening Analytes	Action Levels ¹	Source/ Notes
pH	<6.5 or >9.0	Basin Plan, w/ allowance for elevated pH due to excessive photosynthesis. Elevated pH is especially problematic in combination with high ammonia.
Orthophosphate-P (mg/L)	2.0	USEPA Multi-sector General Permit
Nitrate-N (mg/L)	10.0	Basin Plan, and drinking water standards
Ammonia-N (mg/L)	1.0	Based on Workgroup experience. May also consider unionized ammonia fraction.
Turbidity (NTU)	Best Professional Judgment	WQOs relevant to inland surface waters are not available. Base judgment on channel type and bottom, time since last rain, background levels, and most importantly visual observation (e.g. unusual colors and lack of clarity), and unusual odors.
Temperature (°F or °C)	Best Professional Judgment	Base judgment on season, air temperature, channel type, shading, etc.
Conductivity (µS/cm)	Best Professional Judgment	Values > 5,000 umhos/cm may indicate ICID however, EC may be highly elevated in some regions due to high-TDS groundwater exfiltration to surface water, mineral dissolution, drought, and seawater intrusion. Normal source ID and discharge elimination work is not effective in these situations. Knowledge of area background conditions is important. Values < 750 may indicate excessive potable water discharge or flushing.

Laboratory Analytes	Action Levels	Source/ Notes
MBAS (mg/L)	1.0	Basin Plan, w/ allowance based on Workgroup field experience and possible field reagent interferences
Oil and Grease (mg/L)	15	USEPA Multi-sector General Permit. If a petroleum sheen is observed, the sample should be collected from the water surface. Visual observations may justify immediate investigation.
Diazinon (µg/L)	0.5	Response to diazinon and chlorpyrifos levels above 0.5 µg/L should focus on education and outreach to potential dischargers in the target drainage basin. Highly elevated levels should be investigated aggressively as with other potential ICIDs.
Chlorpyrifos (µg/L)	0.5	
Dissolved Cadmium (µg/L)	California Toxics Rule	Use California Toxics Rule Table, 1-hour criteria to determine appropriate action level for individual samples.
Dissolved Copper (µg/L)	California Toxics Rule	Table provides benchmarks based on hardness and dissolved metals concentration. For example, at 300 mg/L hardness the following action levels would apply: Cd - 14 ppb; Cu - 38 ppb; Pb - 209 ppb; and Zn - 297 ppb.
Dissolved Lead (µg/L)	California Toxics Rule	
Dissolved Zinc (µg/L)	California Toxics Rule	
Total Coliform (MPN/100 mL)	50,000	
Fecal Coliform (MPN/100 mL)	20,000	Action levels are based on upper 90% confidence level of Copermittes 2002 dry weather analytical monitoring data.
Enterococcus (MPN/100 mL)	10,000	

¹The referenced action levels should not be the sole criteria for initiating a source identification investigation. Dry weather monitoring data should be interpreted using a variety of available information including best professional judgment and within-site and between-site sample variability.

Table updated 8-01-02, 9-20-02, 4-3-03, 04-20-04 04-13-2005

What is needed

- Co-Permittees are responsible for validating their data usability.
- Are there data submitted in the regional data sharing that have QA Qualifiers due to field/lab issues?
- Assumption is that all data is valid.
- Create the written plan and standardize with DWMWG.

Thank You!

