

# QAPP AMENDMENT FORM

## IRRIGATED LANDS REGULATORY PROGRAM

COALITION NAME: SAN JOAQUIN COUNTY AND DELTA WATER QUALITY COALITION

WDR ORDER #: R5-2014-0029-R1

QAPP VERSION: 2.0

PREPARED BY: MLJ-LLC

DATE PREPARED: JUNE 16, 2015

### AMENDMENT #1

**TITLE:** Data quality objectives update for acceptable percent recovery limits in Laboratory Control Spikes (LCS) and Matrix Spikes (MS) for methods EPA 200.8 (metals), EPA 8141(organophosphates), EPA 549.2 (paraquat dichloride) and EPA 8270M (sediment pesticides).

**SECTION OF QAPP AFFECTED:** The amendment applies to Table 5 (pages 22-23) of Element 7 (Quality Objectives and Criteria for Measurement Data) in the Quality Assurance Project Plan (QAPP, approved February 23, 2011) and includes an update to the format of the table as well as an update to the laboratory control spike (LCS) and matrix spike (MS) recoveries. Table 5 of the QAPP contains a column for accuracy/recovery, which applies to both LCS and MS acceptable percent recoveries. This amendment separates the single column into two; one for acceptable recovery limits for LCS and MS. The only recovery limits that have changed in values in Table 5 are for the following constituent groups: metals, organophosphates, paraquat dichloride, and sediment pesticides. Acceptable MS and LCS recoveries for constituents that are not included in this amendment have not been applied to the table. The two separate columns in Table 5 for this amendment also reflects that the analysis for method Walkley Black (sediment total organic carbon, TOC) is run with an LCS, but not an MS. In addition, the spelling of the analyte demeton-s was corrected in Table 5. In this amendment, recovery limits that have changed are struck out and updated ranges are highlighted and underlined in Table 5.

**JUSTIFICATION:** The laboratories that analyze Coalition samples routinely conduct internal studies to determine acceptable LCS and MS recovery capabilities. This amendment reflects the acceptable recovery limits determined during the most recent studies conducted in July 2014 by APPL (organophosphates) and in November 2014 by Caltest (metals and sediments pesticides). For paraquat dichloride (analyzed by NCL),

the recovery limits need to be updated to reflect those indicated in the analysis method EPA 549.2. The recovery limits in this amendment meet the percent recovery requirements outlined in the 2008 QAPP guidelines for the Irrigated Land Regulatory Program (ILRP, Order No. R5-2008-0005).

#### *Caltest Analysis - Metals & Sediment Pesticides*

The LCS/MS acceptable percent recovery limits for metals will be increased from 85-115% to 80-120%. The recovery limits of 80-120% are more stringent than the limits within the 2008 MRPP QAPP guidelines (75-125%).

The LCS and MS acceptable percent recovery limits will be updated for the following sediment pesticides: bifenthrin, chlorpyrifos, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin/tralomethrin, esfenvalerate/fenvalerate, fenpropathrin, and permethrin. Within the 2008 QAPP guidelines for the ILRP, the acceptable limits can be 50-150% or control limits at  $\pm 3$  standard deviations based on actual laboratory data. When the laboratory evaluated recovery capabilities in November 2014, new upper and lower percent recovery limits were generated by evaluating recoveries in 49 LCS and 56 MS samples at  $\pm 3$  standard deviations for each sediment pesticide constituent. Therefore, there are separate recovery limits for sediment pesticides in LCS and MS samples in this amendment. The lower acceptable control limits for both LCS and MS samples have increased compared to the current QAPP, with the exception of chlorpyrifos. In both LCS and MS samples, the upper acceptable limits have decreased, except in fenpropathrin and permethrin.

#### *APPL Analysis - Organophosphates*

Within this amendment, the percent recovery limits for all the organophosphates are updated based on the most recent reviews conducted by the laboratory. During the most recent review of recovery capabilities in July 2014, the laboratory used the most recent 30 LCS in batches associated with the Coalition to generate new upper and lower acceptable limits at  $\pm 3$  standard deviations for each organophosphate constituent. The updates to the recovery limits are the same for the both LCS and MS samples for each constituent. The lower acceptable limits have increased for all constituents except dichlorvos and methamidophos and the upper acceptable limits have increased or stayed the same for all constituents except for chlorpyrifos, demeton-s, disulfoton, malathion, phorate, and phosmet. Since, the laboratory established recovery limits at  $\pm 3$  standard deviations for each constituent, the updates made to this amendment meet the requirements in the 2008 QAPP guidelines for the ILRP.

#### *NCL Analysis - Paraquat dichloride*

The acceptable LCS/MS percent recovery limits are updated for paraquat dichloride from 50-141% to 70-130% based on the recommended recovery limits specified in analytical method EPA 549.2. The limits in this amendment also meet the requirements summarized in the 2008 QAPP guidelines (2008 MRPP Attachment C, Appendix B) of 50-150% or control limits at  $\pm 3$  standard deviations.

## DETAIL OF CHANGES:

**Table 1. (Element 7) Data quality objectives for field and laboratory accuracy, precision, and completeness measurements.**

Data quality objectives in measurements of accuracy, precision, and completeness.

Constituent	Matrix	Matrix Spike Frequency <sup>†</sup>	Lab Control Spike Frequency <sup>†</sup>	Matrix Spike Accuracy/ Recovery	Laboratory Control Spike Accuracy/Recovery	Lab Duplicate Frequency <sup>†</sup>	Precision	Completeness
Physical Parameters								
Flow	Fresh Water	NA	NA	±2% NA	NA	1 per batch	±2%	90%
pH	Fresh Water	NA	NA	±0.5 units NA	NA	1 per batch	±0.5 units	90%
Specific Conductivity	Fresh Water	NA	NA	±5% NA	NA	1 per batch	±5%	90%
Dissolved oxygen	Fresh Water	NA	NA	±0.5 mg/L NA	NA	1 per batch	±0.5 mg/L or ±10%	90%
Temperature	Fresh Water	NA	NA	±0.5°C NA	NA	1 per batch	±0.5°C or 10%	90%
Turbidity	Fresh Water	NA	NA	NA	NA	1 per batch	RPD ≤ 20%	90%
Total Dissolved Solids	Fresh Water	NA	NA	NA	NA	1 per batch	RPD ≤ 20%	90%
Total Suspended Solids	Fresh Water	NA	NA	NA	NA	1 per batch	RPD ≤ 20%	90%
Hardness	Fresh Water	1 per batch	1 per batch	80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Total Organic Carbon	Fresh Water	1 per batch	1 per batch	80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Pathogens								
Escherichia coli	Fresh Water	1 per batch	1 per batch	NA	NA	1 per batch	R <sub>log</sub> ≤ 3.27*mean R <sub>log</sub>	90%
Toxicity								
Water Column Toxicity	Fresh Water	1 per batch	1 per batch	NA	NA	1 per batch	RPD ≤ 25%	90%
Sediment Toxicity	Sediment	1 per batch	1 per batch	NA	NA	1 per batch	RPD ≤ 25%	90%
Carbamates								
Aldicarb	Fresh Water	1 per batch	1 per batch	31-133%	31-133%	1 per batch	RPD ≤ 25%	90%
Carbaryl	Fresh Water	1 per batch	1 per batch	44-133%	44-133%	1 per batch	RPD ≤ 25%	90%
Carbofuran	Fresh Water	1 per batch	1 per batch	36-165%	36-165%	1 per batch	RPD ≤ 25%	90%
Methiocarb	Fresh Water	1 per batch	1 per batch	35-142%	35-142%	1 per batch	RPD ≤ 25%	90%
Methomyl	Fresh Water	1 per batch	1 per batch	23-152%	23-152%	1 per batch	RPD ≤ 25%	90%
Oxamyl	Fresh Water	1 per batch	1 per batch	10-117%	10-117%	1 per batch	RPD ≤ 25%	90%
Organochlorines								
DDD	Fresh Water	1 per batch	1 per batch	38-135%	38-135%	1 per batch	RPD ≤ 25%	90%
DDE	Fresh Water	1 per batch	1 per batch	21-134%	21-134%	1 per batch	RPD ≤ 25%	90%
DDT	Fresh Water	1 per batch	1 per batch	18-145%	18-145%	1 per batch	RPD ≤ 25%	90%
Dicofol	Fresh Water	1 per batch	1 per batch	40-135%	40-135%	1 per batch	RPD ≤ 25%	90%
Dieldrin	Fresh Water	1 per batch	1 per batch	48-121%	48-121%	1 per batch	RPD ≤ 25%	90%
Endrin	Fresh Water	1 per batch	1 per batch	24-143%	24-143%	1 per batch	RPD ≤ 25%	90%
Methoxychlor	Fresh Water	1 per batch	1 per batch	30-163%	30-163%	1 per batch	RPD ≤ 25%	90%
Organophosphates								
Azinphos-methyl	Fresh Water	1 per batch	1 per batch	36-189% 30-172%	30-172%	1 per batch	RPD ≤ 25%	90%

Constituent	Matrix	Matrix Spike Frequency <sup>†</sup>	Lab Control Spike Frequency <sup>†</sup>	Matrix Spike Accuracy/ Recovery	Laboratory Control Spike Accuracy/Recovery	Lab Duplicate Frequency <sup>†</sup>	Precision	Completeness
Chlorpyrifos	Fresh Water	1 per batch	1 per batch	61-125% 40-144%	40-144%	1 per batch	RPD ≤ 25%	90%
Diazinon	Fresh Water	1 per batch	1 per batch	57-130% 45-130%	45-130%	1 per batch	RPD ≤ 25%	90%
Dichlorvos	Fresh Water	1 per batch	1 per batch	10-175% 13-161%	13-161%	1 per batch	RPD ≤ 25%	90%
Dimethoate	Fresh Water	1 per batch	1 per batch	68-202% 40-170%	40-170%	1 per batch	RPD ≤ 25%	90%
Demeton-s	Fresh Water	1 per batch	1 per batch	40-125% 35-130%	35-130%	1 per batch	RPD ≤ 25%	90%
Disulfoton	Fresh Water	1 per batch	1 per batch	47-117% 28-131%	28-131%	1 per batch	RPD ≤ 25%	90%
Malathion	Fresh Water	1 per batch	1 per batch	47-125% 30-137%	30-137%	1 per batch	RPD ≤ 25%	90%
Methamidophos	Fresh Water	1 per batch	1 per batch	25-136% 36-124%	36-124%	1 per batch	RPD ≤ 25%	90%
Methidathion	Fresh Water	1 per batch	1 per batch	50-150%	50-150%	1 per batch	RPD ≤ 25%	90%
Parathion, methyl	Fresh Water	1 per batch	1 per batch	55-164%	50-150%	1 per batch	RPD ≤ 25%	90%
Phorate	Fresh Water	1 per batch	1 per batch	44-117% 42-125%	42-125%	1 per batch	RPD ≤ 25%	90%
Phosmet	Fresh Water	1 per batch	1 per batch	50-150% 40-153%	40-153%	1 per batch	RPD ≤ 25%	90%
Herbicides								
Atrazine	Fresh Water	1 per batch	1 per batch	39-156%	39-156%	1 per batch	RPD ≤ 25%	90%
Cyanazine	Fresh Water	1 per batch	1 per batch	22-172%	22-172%	1 per batch	RPD ≤ 25%	90%
Diuron	Fresh Water	1 per batch	1 per batch	52-136%	52-136%	1 per batch	RPD ≤ 25%	90%
Glyphosate	Fresh Water	1 per batch	1 per batch	85.7-121%	85.7-121%	1 per batch	RPD ≤ 25%	90%
Linuron	Fresh Water	1 per batch	1 per batch	49-144%	49-144%	1 per batch	RPD ≤ 25%	90%
Paraquat dichloride	Fresh Water	1 per batch	1 per batch	50-141% 70-130%	70-130%	1 per batch	RPD ≤ 25%	90%
Simazine	Fresh Water	1 per batch	1 per batch	21-179%	21-179%	1 per batch	RPD ≤ 25%	90%
Trifluralin	Fresh Water	1 per batch	1 per batch	40-148%	40-148%	1 per batch	RPD ≤ 25%	90%
Metals								
Arsenic	Fresh Water	1 per batch	1 per batch	85-115% 80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Boron	Fresh Water	1 per batch	1 per batch	85-115% 80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Cadmium	Fresh Water	1 per batch	1 per batch	85-115% 80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Copper	Fresh Water	1 per batch	1 per batch	85-115% 80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Lead	Fresh Water	1 per batch	1 per batch	85-115% 80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Molybdenum	Fresh Water	1 per batch	1 per batch	85-115% 80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Nickel	Fresh Water	1 per batch	1 per batch	85-115% 80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Selenium	Fresh Water	1 per batch	1 per batch	85-115% 80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Zinc	Fresh Water	1 per batch	1 per batch	85-115% 80-120%	80-120%	1 per batch	RPD ≤ 20%	90%
Nutrients								
Total Kjeldahl Nitrogen	Fresh Water	1 per batch	1 per batch	90-110%	NA	1 per batch	RPD ≤ 20%	90%
Nitrate (as N) + Nitrite (as N)	Fresh Water	1 per batch	1 per batch	90-110%	NA	1 per batch	RPD ≤ 20%	90%
Total Ammonia	Fresh Water	1 per batch	1 per batch	90-110%	NA	1 per batch	RPD ≤ 20%	90%
Total Phosphorus	Fresh Water	1 per batch	1 per batch	90-110%	NA	1 per batch	RPD ≤ 20%	90%
Soluble Orthophosphate	Fresh Water	1 per batch	1 per batch	90-110%	NA	1 per batch	RPD ≤ 20%	90%
Sediment Sampling								
Bifenthrin	Sediment	1 per batch	1 per batch	40-160% 31-200%	65-148%	1 per batch	RPD ≤ 25%	90%
Cyfluthrin	Sediment	1 per batch	1 per batch	40-160% 51-149%	51-149%	1 per batch	RPD ≤ 25%	90%
Cypermethrin	Sediment	1 per batch	1 per batch	40-160% 70-152%	63-149%	1 per batch	RPD ≤ 25%	90%
Deltamethrin:Tralomethrin	Sediment	1 per batch	1 per batch	40-160% 31-174%	43-139%	1 per batch	RPD ≤ 25%	90%
Esfenvalerate	Sediment	1 per batch	1 per batch	40-160% 30-175%	58-157%	1 per batch	RPD ≤ 25%	90%
Lambda-Cyhalothrin	Sediment	1 per batch	1 per batch	40-160% 27-164%	44-131%	1 per batch	RPD ≤ 25%	90%

Constituent	Matrix	Matrix Spike Frequency <sup>†</sup>	Lab Control Spike Frequency <sup>†</sup>	Matrix Spike Accuracy/ Recovery	Laboratory Control Spike Accuracy/Recovery	Lab Duplicate Frequency <sup>†</sup>	Precision	Completeness
Permethrin	Sediment	1 per batch	1 per batch	40-160% 30-200%	50-184%	1 per batch	RPD ≤ 25%	90%
Fenpropathin	Sediment	1 per batch	1 per batch	40-160% 48-176%	44-178%	1 per batch	RPD ≤ 25%	90%
Chlorpyrifos	Sediment	1 per batch	1 per batch	40-160% 8-190%	53-131%	1 per batch	RPD ≤ 25%	90%
Total Solids	Sediment	NA	NA	NA	NA	1 per batch	RPD ≤ 25%	90%
Total Organic Carbon	Sediment	NA	1 per batch	75-125% NA	75-125%	1 per batch	RPD ≤ 20%*	90%
Grain Size	Sediment	NA	NA	NA	NA	1 per batch	RPD ≤ 25%	90%

NA-Not applicable.

<sup>†</sup>Either a matrix spike duplicate or a laboratory control spike duplicate may function as the lab duplicate in any batch. A CRM may be used in place of a laboratory control spike.

\*if result > 10x MDL