
Central Valley Regional Water Quality Control Board

15 January 2013

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EAST SAN JOAQUIN WATER QUALITY COALITION AND SAN JOAQUIN COUNTY AND DELTA WATER QUALITY COALITION – MONITORING PROGRAM UPDATES

Thank you for submitting the 26 November 2012 requests to amend the East San Joaquin Water Quality Coalition and the San Joaquin County and Delta Water Quality Coalition (Coalitions) Monitoring and Reporting Program (MRP) Plans, and the Quality Assurance Project Plans (QAPP). The requests for both Coalitions are identical and propose to modify preservation temperature for water and sediment samples, sample holding time for sediment chemistry and total organic carbon analysis, and to update the analytical method for triazines.

Central Valley Regional Water Quality Control Board (Central Valley Water Board) staff reviewed the current U.S. Environmental Protection Agency (EPA) method requirements, and preservation and holding time guidelines presented in the current Title 40 of the Code of Federal Regulations Part 136. Additionally, the Quality Assurance Officer for the Central Valley Water Board reviewed the Quality Control package for triazines supplied by the laboratory contracted by the Coalitions and verified that requirements in MRP Order No. R5-2008-0005 will be met using the method EPA 8141A. Final verification of the method's performance will be determined using recovery rates and other QA/QC data from actual field samples.

Based on the information provided in the request letter and staff's attached memorandum, I approve the Coalitions' request to update their monitoring programs. To effectively complete this transition, please submit amendments to the MRP Plan and QAPP by **15 February 2013**.

If you have any questions or comments regarding this letter, please contact Jelena Hartman at jhartman@waterboards.ca.gov or by phone at 916-464-4628.

[Original signed by]

Pamela C. Creedon
Executive Officer

Enclosure: Staff Review of East San Joaquin Water Quality Coalition Request to Update Monitoring Program

cc: Dr. Michael Johnson, MLJ-LLC
Melissa Turner, MLJ-LLC
Leticia Valadez, Central Valley Regional Water Quality Control Board

Central Valley Regional Water Quality Control Board

TO: Susan Fregien
 Senior Environmental Scientist
 Monitoring and Implementation Unit
 Irrigated Lands Regulatory Program

FROM: Jelena Hartman
 Environmental Scientist
MONITORING AND IMPLEMENTATION UNIT
IRRIGATED LANDS REGULATORY PROGRAM

DATE: 10 January 2013

SUBJECT: EAST SAN JOAQUIN WATER QUALITY COALITION AND SAN JOAQUIN COUNTY AND DELTA WATER QUALITY COALITION REQUEST TO UPDATE MONITORING PROGRAM

The California Regional Water Quality Control Board, Central Valley Region received requests from both the East San Joaquin Water Quality Coalition and the San Joaquin County and Delta Water Quality Coalition (Coalitions) on 26 November 2012 to amend their Monitoring and Reporting (MRP) Plans and Quality Assurance Project Plans (QAPP). Both requests are identical, and propose to update water and sediment sample preservation temperature, initial preservation and hold time for sediment chemistry and total organic carbon (TOC) analysis, and to add EPA 8141A as the analytical method for triazines. The current requirements and proposed changes are summarized in Table 1.

Table 1. Summary of current and proposed changes to sample handling requirements

Requirements	Current	Proposed Change	Ref	Approve?
Preservation Temperature*				
Water / sediment chemistry	store at 4°C	store at ≤6°C	1,2,3	Yes
<i>E. coli</i> analysis	store at 4°C	store at <8°C	1,4	Yes
Initial Preservation and Hold Time				
Sediment TOC	freeze within 48 hr	freeze within 28 days or analyze within 28 days	2	Yes
Sediment chemistry	freeze within 48 hr	freeze within 48 hours or extract within 14 days, analyze within 40 days of extraction	2,3	Yes
Triazine analysis	EPA 619	EPA 8141A	3	Yes

*No change in hold time or other preservation requirements, except for sediment TOC and chemistry

References: ¹Title 40 of the Code of Federal Regulations (CFR) Part 136
²2008 Surface Water Ambient Monitoring Program (SWAMP) QAPP
³2007 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846)
⁴2006 Standard Methods for Examination of Water and Wastewater

Water and sediment sample preservation temperature

The requested water and sediment sample preservation temperature of $\leq 6^{\circ}\text{C}$ is authorized for use in data gathering and environmental monitoring under the Clean Water Act (Title 40 CFR Part 136). The update of the sample handling requirements is consistent with the guidelines in the 2007 edition of *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846) and the 2008 Surface Water Ambient Monitoring Program (SWAMP) QAPP. Staff recommends that water and sediment sample preservation temperature is updated to $\leq 6^{\circ}\text{C}$.

E. coli sample hold temperature

The Monitoring and Reporting Program (MRP) Order No. R5-2008-0005 requires samples for *E. coli* analysis to be stored at 4°C for up to 24 hours. The Coalitions are requesting the sample storage temperature of $< 8^{\circ}\text{C}$ with no change in hold time. The proposed modification of holding temperature meets or exceeds the most recent requirements published in the *Standard Methods for the Examination of Water and Wastewater* for microbiological analysis (SM 9060) and the Title 40 CFR Part 136 which specify a sample holding temperature of $< 8^{\circ}\text{C}$ and $< 10^{\circ}\text{C}$, respectively.

While under both Title 40 CFR Part 136 and under SM 9060 (nonpotable water samples for compliance purposes) the maximum hold time is 8 hours, the holding time up to 24 hours is consistent with the current sample holding requirements and will ensure data comparability. Additionally, published studies suggest that water samples can be stored for periods longer than 8 hours with no significant change in *E. coli* density. Pope et al. (2003)¹ found that sixteen out of 17 surface water samples from a variety of sites across the United States, held below 10°C and not allowed to freeze, could be analyzed using the Colilert method with no significant differences in *E. coli* results up to 24 hours from the time of collection. A more recent investigation found that samples for *E. coli* by Colilert were stable for up to 18 hours (Auelenbach 2010)². Longer hold times can lead to a decrease in bacteria count, and add a negative bias to results.

Staff recommends that the sample hold temperature can be updated to 8°C for the hold time up to 24 hours. The hold time must not be exceeded, and samples should be analyzed as soon as received by the laboratory.

Sediment TOC sample hold time

The MRP Order lists initial preservation up to 48 hours and a maximum holding time of 12 months at -20°C for sediment TOC analysis; hold time until analysis is not specified. The Coalitions propose to update the initial hold time for sediment TOC to 28 days until analysis or freezing, which is identical to requirements in the 2008 SWAMP QAPP. Staff recommends that the hold time for sediment samples for TOC should be 28 days until analysis; samples should be frozen as soon as possible if the analysis cannot be completed within 28 days.

Sediment chemistry sample hold time

The MRP Order lists initial preservation up to 48 hours and a maximum holding time of 12 months at -20°C for sediment chemistry analysis; hold time until extraction and analysis is not

¹ Pope ML, Busses M, Feige MA, Shadix L, Gonder S, Rodgers C, Chambers Y, Pulz J, Miller K, Conner II K, Standridge J. 2003. Assessment of the Effects of Holding Time and Temperature on *Escherichia coli* Densities in Surface Water Samples. *Applied and Environmental Microbiology* 69(10): 6201-6207.

² Auelenbach BT. 2010. Bacteria holding times for fecal coliform by mFC agar method and total coliform and *Escherichia coli* by Colilert®-18 Quanti-Tray® method. *Environmental Monitoring and Assessment* 161: 147-159.

specified. The Coalitions are requesting to add the maximum holding time until extraction of 14 days, and time until analysis of 40 days following the extraction. The Coalitions will retain 48 hours as the initial hold time until freezing unchanged from the current requirement.

The general guidelines in SW-846 recommend that sediment samples for semivolatile organics analyses should be extracted within 14 days and extracts analyzed within 40 days following extraction. Maximum holding time of 14 days until extraction is consistent with the SWAMP requirements for organophosphate pesticides and pyrethroids in sediment. If frozen, samples have identical extraction and analysis requirements following thawing.

Staff verified that the requested hold time for sediment chemistry is consistent with current methods for sediment chemistry analysis, and recommends approval of the proposed updates to the Coalitions' QAPPs.

Method for triazine analysis

The laboratory contracted by the Coalitions (Laboratory in further text) has been analyzing triazines in water using US Environmental Protection Agency (EPA) Method 619, which is listed in the MRP Order as an optional method for triazine analysis. The Coalitions are requesting to add EPA 8141A as the analytical method for atrazine, cyanazine and simazine. Both EPA 619 and 8141 employ gas chromatography (GC) for high resolution separation of compounds, followed by flame ionization with a nitrogen-phosphorus detector. All extracts are confirmed on a second GC column, which must meet all performance criteria.

The EPA method 8141A lists atrazine and simazine as target analytes, and the Laboratory will obtain the California Environmental Laboratory Accreditation Program (CA-ELAP) certification for atrazine and simazine by EPA 8141A in January 2013. The CA-ELAP no longer offers certification for cyanazine by any method. In the absence of the State Department of Health Services certification for cyanazine, the MRP Order requires the Laboratory to follow steps for noncertified laboratories. The request included a quality control package for triazines prepared by the Laboratory (results are summarized in Table 2). The submitted validation package for triazines was examined by the Quality Assurance Officer for the Central Valley Regional Water Quality Control Board, Ms. Leticia Valadez.

The initial calibration for cyanazine was performed on 24 October 2012 using eight concentrations ranging from 0.02 to 10 µg/L. Because the derived calibration factors did not meet method requirements, linear regression equations were calculated (Table 2). Linear regression models for both columns were suitable for quantitative purposes. A method blank sample demonstrated that the process and system were free of contamination. Results from the Method detection limit (MDL) study demonstrated MDL's approximately 4 times lower than the required reporting limit of 0.5 µg/L. The second source calibration verification, initial precision and recovery, and a continuing calibration check passed for both columns. Surrogate recoveries ranged from 88 to 117%, and met method requirements.

Staff recommends approval of the request to add EPA 8141A as the method for atrazine, cyanazine and simazine analysis. The EPA method 8141A is widely accepted, and the Laboratory will obtain the CA-ELAP certification, for analysis of atrazine and simazine. The Coalitions provided sufficient information for staff to verify that the EPA 8141A will meet the performance requirements for cyanazine analysis. However, while controlled laboratory samples can meet QA/QC requirements, matrix interferences can occur when field samples are analyzed. Therefore, the final validation of the method's performance will be based on field samples and associated QA/QC results. Recovery rates for the MS/MSD and other QA/QC

information will be used to determine if the method can perform as the validation data for controlled laboratory samples indicate.

Table 2. Initial demonstration of performance for analysis of cyanazine using EPA 8141A.

Category/Criteria	Column 1	Column 2	Pass?
Initial Calibration			
Calibration Factor RSD<20%	33%	46%	x
Linear regression $r^2 > 0.990$	0.995	0.999	✓
Second source calibration verification			
% Recovery (100±15%)	90%	98%	✓
% Surrogate recovery	88-101%	90-104%	✓
Method Blank			
Result	ND	ND	✓
% Surrogate recovery	93-96%	81-83%	✓
Method Detection Limit (spike = 1 µg/L, n=7)			
Method Detection Limit=SD·3.14	0.121	0.110	✓
Initial Precision and Recovery (spike = 1 µg/L, n=4)			
Average % recovery	103%	101%	✓
% RSD	4.0%	4.2%	✓
% Surrogate recovery	94-112%	99-119%	✓
Ongoing Precision and Recovery (spike = 1 µg/L)			
% Recovery (100±15%)	101%	110%	✓
% Surrogate recovery	100-110%	104-117%	✓

cc: Chris Jimmerson, Central Valley Regional Water Quality Control Board