March 13, 2019

Dear ELAP-Accredited Laboratories,

The California Regional Water Quality Control Board - Central Valley Region (Central Valley Water Board) has adopted a Pyrethroid TMDL and Basin Plan Amendment that sets concentration goals for six pyrethroids in wastewater effluent and surface water. The Basin Plan Amendment (BPA) applies to municipal and agricultural discharges throughout the Central Valley. The BPA, which took effect on February 19, 2019, requires dischargers to begin monitoring for pyrethroids 2020 or sooner. The BPA sets low concentration goals for pyrethroids in discharge and receiving water, and therefore lower analytical reporting limits than commonly commercially available will be required for compliance monitoring. The minimum reporting levels (MRLs)[1] derived from the BPA are specified in Table 1. The Central Valley Water Board is requesting that laboratories submit performance-based method validation packages for analytical methods that can achieve these MRLs for pyrethroids in whole water (unfiltered) samples from surface waters and wastewater effluent. If chronic-based MRLs cannot be achieved, then acute-based MRLs will be accepted on an individual analyte basis. The Central Valley Water Board will consider methods for single laboratory use, but ultimately seeks a method that can be used statewide.

Laboratories interested in participating in compliance monitoring for the BPA must be accredited by the Environmental Laboratory Accreditation Program (ELAP). The Central Valley Water Board will review each validation package, and upon approval, the submitting laboratory will be eligible for accreditation under ELAP. Approved laboratories should then submit an amendment application for ELAP accreditation of the method. The Central Valley Water Board and ELAP will work closely to reduce the duration of the approval and accreditation process.

40 CFR 136 lists the following EPA-approved analysis methods for determining Clean Water Act compliance for permethrin: 608.2, 508, 525.1, 525.2, 1656, 1660, 608.3, and 625.1. Validation packages for an alternative test procedure or new method for total permethrin analysis will require US EPA approval. The other pyrethroids included in the BPA are not listed in 40 CFR 136, and therefore, the Central Valley Water Board has the authority to approve and will consider all validated methods for these analytes.

Validation packages should be prepared in accordance with EPA guidance for review and validation of alternative or new methods (USEPA, 2018a&b). The Central Valley Water Board requests that applicants complete and return the attached questionnaire to indicate their intent to participate in the method validation.

[1] MRLs represent the lowest concentration of a compound that can be quantitatively measured within prescribed quality control limits (USEPA, 2010).

Participating laboratories should submit their questionnaire to the Central Valley for review by April 15, 2019. Applicants should submit completed application packages to the Central Valley Water Board by September 30, 2019. Both the questionnaire and application package should be submitted to jessica.mullane@waterboards.ca.gov Validation packages will be reviewed on an ongoing basis, but priority will be given to those received by these deadlines.

Additional information may be provided to laboratories as the process continues. If you have any questions or would like to discuss, please contact Jessica Mullane at (916) 464-4691 or jessica.mullane@waterboards.ca.gov or Danny McClure at (916) 464-4751 or daniel.mcclure@waterboards.ca.gov.

Sincerely,

Original signed by
Daniel J. McClure, P.E.
Senior Water Resource Control Engineer
Central Valley Regional Water Quality Control Board

cc: Andrew Hamilton, ELAP, Division of Drinking Water, SWRCB
Melissa Morris, Office of Information Management and Analysis, SWRCB

Validation Package Requirements

Validation packages for both new and alternative methods must include the standardized quality control tests found in Appendix G of the EPA protocols. More detailed guidance on these tests when developing new methods can be found in Appendix G of USEPA, 2018b. Modified or alternative methods are required to meet or improve upon the quality control criteria specified in the original method.

Validation packages must include matrix effect samples to demonstrate that performance criteria can be met in the appropriate environmental matrix (wastewater and/or surface water) as well as reagent water or reference matrix. The measurement quality objectives that the Central Valley Water Board requires are summarized in Table 2.

1. Calibration linearity
The Central Valley Water Board requires a minimum of five calibration points and an $r \geq 0.995$ to demonstrate linearity. The five standards should span the expected sample range for each analyte, with the lowest calibration point below the MRL. Laboratories must include all calculations in the validation packages.

2. Calibration verification
The Central Valley Water Board requires 80-120% recovery of analytes in a mid-level calibration verification standard. Laboratories must include all calculations in the validation packages.

3. Absolute and relative retention time windows (for chromatographic analyses)
The Central Valley Water Board has no parameters for this component. Laboratories must include these values and the associated calculations for each analyte.

4. Initial precision and recovery (IPR)
Alternative Method
Laboratories must demonstrate their ability to meet or exceed the IPR precision and recovery criteria given for the EPA-approved reference method using both the alternative method and the corresponding approved method. If the reference method has no acceptance criteria, laboratories must demonstrate a recovery of 50-150% and a relative standard deviation (RSD) of less than 35%. Laboratories must perform the IPR test by analyzing four replicates of reagent water spiked with the analytes of interest. This IPR test should be performed for both the alternative method and the corresponding approved method.

New Method
The Central Valley Water Board requires a recovery of 50-150% and a relative standard deviation (RSD) of less than 35%. Laboratories must perform the IPR test in both a reference matrix (reagent water) and the sample matrix of interest. Laboratories must perform the IPR test by analyzing four replicates of reagent water spiked with the analytes of interest. Laboratories must use a concentration between one and five times the minimum level (ML) of quantitation of the new method and state this concentration in the method. Laboratories should analyze four spiked replicates of the matrix type to which the new method will be applied. The replicate samples should be spiked with the analytes of interest at a concentration one to five times the background concentration of the analytes in the sample or at one to five times the ML, whichever is greater.

5. Ongoing precision and recovery (OPR) (laboratory control sample)

Alternative Method

Laboratories must demonstrate that the alternative method can meet the OPR recovery criteria given in the EPA-approved reference method or 50-150% recovery and an RSD of less than 35%, whichever is more sensitive.

New Method

The Central Valley Water Board requires demonstration of ongoing precision and recovery in the form of a laboratory control sample (LCS). The recovery for this sample must be between 50-150% with an RSD of less than 35%. Laboratories must spike the LCS with the same concentration as that of the IPR samples.

6. Analysis of blanks

The Central Valley Water Board requires laboratories to demonstrate that the analyte concentrations in blank samples are below the requested MRL (Table 1).

7. Surrogate or labeled compound recovery

The Central Valley Water Board requires a surrogate recovery of 50-150% or better. Laboratories may submit historical control limits if available. Laboratories must identify the surrogates used and ensure its relevance to the analytes of interest.

8. Matrix spike and matrix spike duplicate precision and recovery (for non-isotope dilution analyses)

Alternative Method

Laboratories must demonstrate that the alternative method can meet the MS/MSD recovery and precision criteria associated with the EPA-approved reference method or the Central Valley Water Board criteria (Table 2), whichever is more sensitive. Laboratories must perform MS/MSD analysis for each matrix type. If acceptance criteria are not stated in the method, laboratories must demonstrate a recovery of 50-150% and a relative percent difference (RPD) of less than 35%.

New Method

The Central Valley Water Board requires a MS/MSD recovery of 50-150% and a relative percent difference (RPD) of less than 35%. Laboratories should spike the MS and MSD at a level that results in the concentration of the target analytes being at the MRL, one to five times the background concentration of a matrix sample, or at the level specified in the method, whichever is greater.

9. Method detection limit demonstration

Laboratories must perform a method detection limit (MDL) study for alternative and new methods. For both alternative and new methods, the MDL must be lower than the acute-based MRLs listed in Table 1.

Alternative methods must achieve an MDL that is less than or equal to the minimum level (ML) of the EPA-approved reference method, or less than 1/10 the regulatory compliance limit, whichever is greater. Laboratories must perform the MDL study in accordance with the with most recent MDL study requirements published in Appendix B of 40 CFR Part 136. As of August 2017, 40 CFR Part 136 Appendix B requires laboratories to analyze of a minimum of seven spiked samples and seven blanks to determine an MDL.

10. Minimum reporting limit verification
A minimum reporting limit (MRL) test must be performed either concurrently with MDL test or in a separate study. Laboratories must be able to demonstrate 50-150% recovery for samples spiked at the MRL for individual analytes (Table 1).

11. Standard operating procedure
Laboratories must include their standard operating procedure written in the EPA method.

Table 1. Requested minimum reporting levels (MRLs) calculated from BPA concentration goals[1]

Chemical[2]	**Requested MRL[3,4], Acute-Based (ng/L)**	**Requested MRL Chronic-Based, (ng/L)**
Bifenthrin	**1.3**	**0.2**
Cyfluthrin	**1.3**	**0.3**
Cypermethrin	**1.7**	**0.5**
Esfenvalerate	**3.3**	**0.5**
Lambda-cyhalothrin	**1.2**	**0.5**
Permethrin (total)	**10**	**1.7**

[1] See supplemental information for background information about the derivation of the MRL values from the Basin Plan Amendment concentration goals.
[2] Concentrations are total analyte concentrations, including all isomers.
[3] MRL is based on a Measurement Quality Objective (MQO) of 50%-150% recovery of spiked concentrations. Therefore, at or above the MRL, laboratories should obtain 50%-150% recovery or better (USEPA, 2010).
[4] Numbers reported to two significant figures.

Table 2. Quality Control Pyrethroids in Whole Water[1]

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Tuning[2]	Per laboratory SOP	Per laboratory SOP
Calibration	Daily, or just prior to analysis; five or more standards spanning the sample result range[3], with the lowest standard at or below the MRL	r ≥0.995 (or r^2 ≥0.995, all curve types not forced through origin)
Calibration Verification	Per 10 analytical samples[4]	80-120%[5]
Laboratory Blank	Per 20 samples or per analytical batch, whichever is more frequent	<MRL for target analyte
Laboratory Control Sample[6]	Per 20 samples or per analytical batch, whichever is more frequent	50-150%
Matrix Spike	Per 20 samples or per analytical batch, whichever is more frequent	50-150%
Matrix Spike Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	50-150%; RPD <35%
Surrogate[7]	Included in all samples and all QC samples	50-150% or better
Internal Standard	Included in all samples and all QC samples	Per laboratory procedure

[1]Modified from SWAMP's Quality Control and Sample Handling Tables: Synthetic Organic Compounds in Fresh and Marine Water (SWRCB, 2013).

[2]Mass spectrometry only

[3]Sample results above the highest standard are to be diluted and re-analyzed.

[4]Analytical samples include samples only and do not include clean-out or injection blanks.

[5]Limit applies to a mid-level standard; low-level calibration checks near the reporting limit may have a wider range that is project -specific

[6]Laboratory control samples must be matrix-specific.

[7]Laboratory historical limits for surrogate recovery may be submitted if available.

[8]A technical group consisting of regional, laboratory, and research representatives determined that field blanks do not provide technical value to a pyrethroids data set.

Supplemental Information

The concentration goals established in the BPA for bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, and permethrin are freely dissolved concentrations, which are calculated from the whole water concentration following an equation described in the BPA Staff Report. As explained in Section 5.2.2 of the Staff Report, the freely dissolved pyrethroid concentration typically ranges from 1-30% of the whole water concentration, so the requested minimum reporting levels (MRLs) are adjusted upward to account for that.

The MRLs should be set at a level that captures the lower limit of the whole water concentration ranges. The requested method whole water concentrations were calculated and reported to two significant figures using the following equation, accounting for this proposed accuracy and assuming 30% freely dissolved concentration:

$$Whole\ Water\ Concentration = \left(\frac{BPA\ Concentration\ Goals}{30\%}\right) * 50\%$$

References

1. USEPA, 2018a. Protocol for Review and Validation of Alternate Test Procedures for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program. U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. Washington, DC EPA 821-B-18-002. Available online from: https://www.epa.gov/sites/production/files/2018-03/documents/chemical-atp-protocol_feb-2018.pdf.

2. USEPA, 2018b. Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program. U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. Washington, DC EPA 821-B-18-001. Available online from: https://www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol_feb-2018.pdf.

3. USEPA, 2010. Technical Basis for the Lowest Concentration Minimum Reporting Level (LCMRL) Calculator. U.S. Environmental Protection Agency. Office of Water, EPA 815-R-11-001. Available online from: https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100J7CA.txt.

4. SWRCB, 2013. Quality Control and Sample Handling Tables: Synthetic Organic Compounds in Fresh and Marine Water. California State Water Resources Control Board. Surface Water Ambient Monitoring Program (SWAMP). Sacramento, CA. Available online from: https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/syn_org_com_water.pdf.