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## Central Valley Regional Water Quality Control Board

24 September 2021

Environmental Laboratory Technical  
Advisory Committee

Dear ELAP-Accredited Laboratories,

The California Regional Water Quality Control Board - Central Valley Region (Central Valley Water Board) requires dischargers to monitor pesticides that pose a threat to the beneficial uses of Central Valley waterways. In the Central Valley Water Board's Irrigated Lands Regulatory Program (ILRP), a process was established to evaluate pesticides applied by agricultural permittees. This process, referred to as the Pesticide Evaluation Protocol (PEP), uses toxicity, chemical fate, amounts applied, and other information to identify high risk pesticides that warrant monitoring. The PEP process uses toxicity thresholds that are protective of aquatic life and human health. Through the PEP process, ILRP permittees commonly identify imidacloprid, a neonicotinoid pesticide, as a pesticide to monitor during surface water monitoring efforts. When a pesticide warrants monitoring, laboratories should utilize analytical methods that have reporting limits that are less than (ideally) or equal to the most protective toxicity threshold. In the case of imidacloprid, that threshold is 0.01 µg/L (USEPA, 2020 and UC Davis, 2019). However, there are no analytical methods approved in 40 CFR 136 nor published by a voluntary consensus standard body (e.g., Standard Methods, ASTM) for the analysis of neonicotinoids in water, so it is unknown whether analytical methods used by laboratories to analyze these neonicotinoids have reporting limits at or below the threshold limits. Therefore, the Central Valley Water Board is requesting that laboratories submit performance-based method validation packages for analytical methods that can achieve the desired Minimum Reporting Level (MRL) for imidacloprid in whole water (unfiltered) samples from surface waters and wastewater effluent. The desired MRL<sup>1</sup> for imidacloprid is specified in Item 12 below. 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 ILRP must be accredited by the Environmental Laboratory Accreditation Program (ELAP). Prior to obtaining accreditation to test for imidacloprid, the laboratory must submit a validation package to the Central Valley Water Board for approval. 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 must then submit an

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

[amendment application](#)<sup>2</sup> 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.

Imidacloprid is not listed as a parameter of interest in 40 CFR 136 and is considered a state-specific monitoring parameter. Therefore, validation packages do not require submission of an Alternative Testing Procedure (ATP) application for US EPA approval. The Central Valley Water Board has the authority to approve and will consider all validated methods for imidacloprid.

Validation packages should be prepared in accordance with EPA guidance for review and validation of [alternative](#)<sup>3</sup> or [new](#)<sup>4</sup> methods (USEPA, 2018a&b). The validation package requirements are attached to this request letter. Laboratories interested in participating should submit completed validation packages to the Central Valley Water Board by 24 December 2021. The validation package should include a transmittal letter containing the laboratory name and address, laboratory director name, and a point of contact name, phone number, and email address. Validation packages will be reviewed on an ongoing basis, but priority will be given to those received by this deadline.

Additional information may be provided to laboratories as the process continues. If you have any questions or would like to discuss, please contact Chris Jimmerson at [chris.jimmerson@waterboards.ca.gov](mailto:chris.jimmerson@waterboards.ca.gov) or (916) 464-4859 or Susan Fregien at [susan.fregien@waterboards.ca.gov](mailto:susan.fregien@waterboards.ca.gov) or (916) 464-4813.

Sincerely,

*Original signed by*

Susan Fregien  
Senior Environmental Scientist  
Central Valley Regional Water Quality Control Board

cc: Andrew Hamilton, Office of Information Management and Analysis, SWRCB  
Melissa Morris, Office of Information Management and Analysis, SWRCB  
Christopher Hand, Environmental Laboratory Accreditation Program, SWRCB

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<sup>2</sup> Available online at: [www.waterboards.ca.gov/drinking\\_water/certlic/labs/apply.html](http://www.waterboards.ca.gov/drinking_water/certlic/labs/apply.html)

<sup>3</sup> Available online at:  
[www.epa.gov/sites/production/files/2018-03/documents/chemical-atp-protocol\\_feb-2018.pdf](http://www.epa.gov/sites/production/files/2018-03/documents/chemical-atp-protocol_feb-2018.pdf)

<sup>4</sup> Available online at:  
[www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol\\_feb-2018.pdf](http://www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol_feb-2018.pdf)

## 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](#).<sup>5</sup> 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 (surface water and/or wastewater) as well as reagent water or reference matrix. The measurement quality objectives that the Central Valley Water Board requires are summarized in Table 1.

### 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 at or below the MRL. Laboratories must include all calculations in the validation packages.

### 2. Calibration verification

The Central Valley Water Board requires 70-130% 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 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

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<sup>5</sup> Available online at:

[www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol\\_feb-2018.pdf](http://www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol_feb-2018.pdf)

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 (See Item 12).

## **7. Surrogate or labeled isotope dilution standard recovery**

The Central Valley Water Board requires the use of surrogate or labeled isotope dilution standards. If laboratories use surrogates, the laboratories must identify the surrogates used and ensure its relevance to the analytes of interest. Recoveries for surrogates or labeled isotope dilution standards must be 50-150% or better and reported for each analytical sample. The Central Valley Water Board will consider alternate historical control limits if available.

## **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 1), 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 chronic-based MRL in Item 12.

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 revision 2 of the Procedure for the Determination of the Method Detection Limit ([US EPA, 2016](#)<sup>6</sup>) published in Appendix B of 40 CFR Part 136.

## **10. Minimum reporting level verification**

A minimum reporting level (MRL) test must be performed either concurrently with the MDL study or in a separate study. Laboratories must be able to demonstrate 50-150% recovery for samples spiked at the MRL for imidacloprid (see Item 12).

## **11. Standard operating procedure**

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

## **12. Requested Minimum Reporting Level**

The requested Minimum Reporting Level (MRL) for imidacloprid is 0.01 µg/L. This is based on a chronic threshold for the protection of aquatic life in fresh water. 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](#)<sup>7</sup>).

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<sup>6</sup> Available online at:  
[www.epa.gov/sites/default/files/2016-12/documents/mdl-procedure\\_rev2\\_12-13-2016.pdf](http://www.epa.gov/sites/default/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf)

<sup>7</sup> Available online at: [nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100J7CA.txt](http://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100J7CA.txt)

**Table 1. Quality Control Imidacloprid in Whole Water<sup>1</sup>**

<b>Laboratory Quality Control</b>	<b>Frequency of Analysis</b>	<b>Measurement Quality Objective</b>
Tuning <sup>2</sup>	Per laboratory SOP	Per laboratory SOP
Calibration	Per laboratory SOP or method requirements; five or more standards spanning the sample result range, <sup>3</sup> with the lowest standard at or below the MRL	$r \geq 0.995$ (or $r^2 \geq 0.995$ , all curve types not forced through origin)
Calibration Verification	Beginning and end of each batch and per 10 analytical samples <sup>4</sup>	70 – 130% <sup>5</sup>
Laboratory Method Blank	Per 20 samples or per analytical batch, whichever is more frequent	< MRL for target analyte
Laboratory Control Sample <sup>6</sup>	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 or Labeled compound <sup>7</sup>	Included in all samples and all QC samples	50 – 150% or better
Internal Standard, if utilized	Included in all samples and all QC samples	Per laboratory SOP or method requirements

<sup>1</sup> Modified from SWAMP's Quality Control and Sample Handling Tables: Synthetic Organic Compounds in Fresh and Marine Water ([SWRCB, 2013](http://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/syn_org_com_water.pdf)).  
<[www.waterboards.ca.gov/water\\_issues/programs/swamp/docs/mqo/syn\\_org\\_com\\_water.pdf](http://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/syn_org_com_water.pdf)>

<sup>2</sup> Mass spectrometry only

<sup>3</sup> Sample results above the highest standard are to be diluted and re-analyzed.

<sup>4</sup> Analytical samples include samples only and do not include clean-out or injection blanks.

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

<sup>6</sup> Laboratory control samples must match the matrix-type (water/soil/etc.).

<sup>7</sup> Laboratory historical limits for surrogate recovery may be submitted if available.

## References

1. USEPA, 2020. [Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides](https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk). U.S. Environmental Protection Agency. Office of Pesticide Programs. Washington, DC. Available online from: [www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk](https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk).
2. 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](https://www.epa.gov/sites/production/files/2018-03/documents/chemical-atp-protocol_feb-2018.pdf). U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. Washington, DC EPA 821-B-18-002. Available online from: [www.epa.gov/sites/production/files/2018-03/documents/chemical-atp-protocol\\_feb-2018.pdf](https://www.epa.gov/sites/production/files/2018-03/documents/chemical-atp-protocol_feb-2018.pdf).
3. 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](https://www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol_feb-2018.pdf). U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. Washington, DC EPA 821-B-18-001. Available online from: [www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol\\_feb-2018.pdf](https://www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol_feb-2018.pdf).
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5. USEPA, 2010. [Technical Basis for the Lowest Concentration Minimum Reporting Level \(LCMRL\) Calculator](https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100J7CA.txt). U.S. Environmental Protection Agency. Office of Water, EPA 815-R-11-001. Available online from: [nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100J7CA.txt](https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100J7CA.txt).
6. SWRCB, 2013. [Quality Control and Sample Handling Tables: Synthetic Organic Compounds in Fresh and Marine Water](https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/syn_org_com_water.pdf). California State Water Resources Control Board. Surface Water Ambient Monitoring Program (SWAMP). Sacramento, CA. Available online from: [www.waterboards.ca.gov/water\\_issues/programs/swamp/docs/mqo/syn\\_org\\_com\\_water.pdf](https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/syn_org_com_water.pdf).
7. UC Davis, 2019. [Water Quality Criteria Report for Imidacloprid. Phase III: Application of the pesticide water quality criteria methodology](https://www.waterboards.ca.gov/centralcoast/water_issues/programs/tmdl/docs/pesticide_criteria/imidacloprid_report_final_062519.pdf). Prepared for the Central Coast Regional Water Quality Control Board. University of California, Davis. Available online from: [www.waterboards.ca.gov/centralcoast/water\\_issues/programs/tmdl/docs/pesticide\\_criteria/imidacloprid\\_report\\_final\\_062519.pdf](https://www.waterboards.ca.gov/centralcoast/water_issues/programs/tmdl/docs/pesticide_criteria/imidacloprid_report_final_062519.pdf).