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## Los Angeles Regional Water Quality Control Board

April 26, 2024

Dear ELAP-Accredited Laboratories,

The California Regional Water Quality Control Board, Los Angeles Region (Los Angeles Water Board) permits the discharge of effluent from the Hyperion Water Reclamation Plant (WRP) and the Edward C. Little Water Reclamation Facility (ECLWRF) to the Pacific Ocean under the National Pollutant Discharge Elimination System (NPDES) program. The NPDES permit for the Hyperion WRP, which became effective on May 1, 2023, contains an annual monitoring requirement of effluent for flame retardants, including nine polybrominated diphenyl ethers (PBDE) and three organophosphate esters. These pollutants have been added to the monitoring and reporting program as a result of the United States Environmental Protection Agency's consultation with the National Oceanic and Atmospheric Administration (NOAA), National Marine Fisheries Service (NMFS), since these pollutants can accumulate in threatened and endangered species, and in essential fish habitat. These same pollutants are also incorporated into the ECLWRF NPDES permit, which became effective on February 1, 2024.

The targeted minimum reporting levels (MRLs) for these pollutants are specified in Table 1. The Los Angeles Water Board is requesting for laboratories to submit performance-based method validation packages for analytical methods that can achieve the MRLs for flame retardants in whole water (unfiltered) samples from wastewater effluent. The Los Angeles 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 Hyperion WRP, ECLWRF and any other wastewater facilities that discharge flame retardants into the Pacific Ocean must be accredited by the Environmental Laboratory Accreditation Program (ELAP). The Los Angeles Water Board in consultation with ELAP 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.

Analytical methods for the flame retardants in the Hyperion WRP and ECLWRF NPDES permits are not listed in section 136 of Title 40 of the Code of Federal Regulations (40 CFR) and therefore, the Los Angeles Water Board has the authority to consider and approve 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 Los Angeles Water

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NORMA CAMACHO, CHAIR | SUSANA ARREDONDO, EXECUTIVE OFFICER

Board requests that applicants complete and return the attached questionnaire to indicate their intent to participate in the method validation.

Participating laboratories should submit their questionnaire to the Los Angeles Water Board for review by May 27, 2024. Applicants should submit completed application packages to the Los Angeles Water Board by November 25, 2024. Both the questionnaire and application package should be submitted to [adam.taing@waterboards.ca.gov](mailto:adam.taing@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 Adam Taing at (213) 576-6752 or [adam.taing@waterboards.ca.gov](mailto:adam.taing@waterboards.ca.gov) or me at (213) 576-6616 or [jeong-hee.lim@waterboards.ca.gov](mailto:jeong-hee.lim@waterboards.ca.gov).

Sincerely,

Jeong-Hee Lim, Ph.D., P.E.  
Manager, Watershed Regulatory Section

cc: Andrew Hamilton, Ranita Prasad, SWRCB, Office of Information Management  
and Analysis  
Christopher Hand, SWRCB Division of Drinking Water, ELAP

## 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) as well as reagent water or reference matrix. The measurement quality objectives that the Los Angeles Water Board requires are summarized in Table 2. Laboratories must also comply with all ELAP requirements for quality systems defined in the California Code of Regulations (CCR) Title 22 section 64802.05(a).

### 1. Calibration linearity

The Los Angeles Water Board requires a minimum number of calibration points consistent with the 2016 TNI standard, Volume 1 Module 4 section 1.7. Calibration shall be verified using Relative Standard Error (RSE) consistent with the TNI standard. RSE values should be  $\leq 20\%$  for good performing compounds, but must be  $\leq 30\%$  for all analytes. The 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 Los Angeles Water Board requires 80-120% recovery of analytes in a calibration verification standard at or below the mid-point of the calibration range. Laboratories must include all calculations in the validation packages.

### 3. Absolute and relative retention time windows (for chromatographic analyses)

The Los Angeles 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 should demonstrate a recovery of 50-150% and a relative standard deviation (RSD) of less than 30%. Recoveries outside of these ranges may be considered if documentation with explanations is included and acceptable explanation is provided. 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 Los Angeles Water Board requires a recovery of 50-150% and a relative standard deviation (RSD) of less than 30%. 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 of quantitation (ML) of the new method and state this concentration in the method. The ML is also known as the minimum reporting level (MRL) and is defined as the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. 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 30%, whichever is more sensitive.

### New Method

The Los Angeles 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 30%. Laboratories must spike the LCS with the same concentration as that of the IPR samples.

## **6. Analysis of blanks**

The Los Angeles 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 Los Angeles 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 Los Angeles 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 30%.

### New Method

The Los Angeles 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 an 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 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 a minimum of seven spiked samples and seven blanks to determine an MDL.

## **10. Minimum reporting limit verification**

A 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) or the acceptance criteria for recovery outlined in the method.

## **11. Standard operating procedure**

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

**Table 1. Requested minimum reporting levels (MRLs)**

<b>Chemical</b>	<b>CAS No.</b>	<b>Requested MRL<sup>3,4,5</sup> (ng/L)</b>
Polybrominated diphenyl ether (PBDE) 28	41318-75-6	<b>5</b>
PBDE 47	5436-43-1	<b>5</b>
PBDE 99	60348-60-9	<b>5</b>
PBDE 100	189084-64-8	<b>5</b>
PBDE 153	68631-49-2	<b>5</b>
PBDE 183	207122-16-5	<b>5</b>
PBDE 209	1163-19-5	<b>500</b>
tris(1,3-dichloro-2-propyl)phosphate (TDCPP)	13674-87-8	<b>1</b>
tris(2-chloroethyl)phosphate (TCEP)	115-96-8	<b>1</b>
tris(1-chloro-2-propyl)phosphate (TCPP)	13674-84-5	<b>1</b>

<sup>3</sup> 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>4</sup> Values reported to two significant figures.

<sup>5</sup> A lower MRL for PBDE 209 is desired.

**Table 2. Quality Control PBDE and Organophosphate Esters in Wastewater**

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Tuning <sup>2</sup>	Per laboratory SOP	Per laboratory SOP
Calibration	Per laboratory SOP, or just prior to analysis; standards spanning the sample result range <sup>3</sup> , with the lowest standard at or below the MRL	RSE ≤20% or ≤30% for poor performing compounds
Calibration Verification	Per 10 analytical samples <sup>4</sup>	80-120% <sup>5</sup>
Laboratory 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 <30%
Surrogate <sup>7</sup>	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

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

<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 be matrix-specific.

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

## 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](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](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?Dockkey=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](https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/mqo/syn_org_com_water.pdf).