Karen Morrison
Director

Department of Pesticide Regulation

Gavin Newsom
Governor

Yana Garcia
Secretary for Environmental Protection

M E M O R A N D U M

TO: Joy Dias
Environmental Program Manager I

FROM: Vaneet Aggarwal *Original Signed by*
Senior Environmental Scientist
916-445-3870

DATE: July 28, 2025

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-061 AS UNEQUIVOCAL ACCORDING TO THE PESTICIDE CONTAMINATION PREVENTION ACT

BACKGROUND

The Pesticide Contamination Prevention Act (Food and Agricultural Code [FAC] sections 13141 et seq.) was passed in 1985 to prevent further pesticide pollution of groundwater that may be used for drinking water supplies. FAC section 13149 specifies the conditions under which a pesticide or degradate is considered detected in groundwater, and thus subject to formal review as specified. FAC subsection 13149(d) allows a finding of a pesticide or degradate in groundwater to be based on a single analytical method conducted by a single analytical laboratory if the analytical method approved by the Department of Pesticide Regulation (DPR) provides unequivocal identification of a chemical. DPR's process for qualifying methods that provide unequivocal identification of a chemical is included in the memo entitled "Evaluating analytical methods for compliance with the Pesticide Contamination Prevention Act requirements" (Aggarwal, 2012). The memo describes that a method is deemed unequivocal if it meets specific selectivity and/or structural analysis factors. This qualification memo serves to establish if the method EMON-SM-05-061 (CDFA, 2025) is unequivocal according to the Pesticide Contamination Prevention Act.

PURPOSE

Determine if the analytical method EMON-SM-05-061 (CDFA, 2025) for azoxystrobin acid, bensulfuron-methyl, bispyribac sodium, clomazone, halosulfuron methyl, 2-methyl-4-chlorophenoxyacetic acid (MCPA), molinate, orthosulfamuron, penoxsulam, propanil, propiconazole, thiobencarb, and triclopyr in groundwater used by the California Department of Food and Agriculture (CDFA) meets the definition of an unequivocal method.

DISCUSSION AND RECOMMENDATION

The CDFA Center for Analytical Chemistry method EMON-SM-05-061 (CDFA, 2025) uses a liquid chromatograph coupled to a tandem mass spectrometer (LC/MS/MS) for the detection of the 13 analytes listed in Table 1. Prior to injection of a sample into the LC/MS/MS, a measured mass of groundwater sample (250 g) is acidified with 3N hydrochloric acid (HCl) and passed through a solid phase extraction cartridge (Waters Oasis® HLB 6 cc, 200 mg). The analytes are then eluted with 5.0 mL of acetonitrile/methanol (50/50 (v/v)) solution and the eluant is concentrated to ~ 0.5 mL under a gentle stream of nitrogen in a water bath. The eluant is then brought up to a final volume of 1.0 mL with acetonitrile/methanol (50/50 (v/v)) solution. The extract is then analyzed by LC/MS/MS. Two surrogates; 2,4,5-T and simazine-d_{10} are used to verify extraction efficiency.

Table 1. Pesticides determined by LC/MS/MS in CDFA Method EMON-SM-05-061.

Azoxystrobin acid	Orthosulfamuron
Bensulfuron-methyl	Penoxsulam
Bispyribac sodium	Propanil
Clomazone	Propiconazole
Halosulfuron methyl	Thiobencarb
MCPA	Triclopyr
Molinate	

A method is considered “unequivocal” based on

(a) matching retention time of the certified reference standard,
(b) the presence of the precursor ion at the retention time, and/or
(c) the presence of one or more characteristic product ions (Aggarwal, 2012).

For the 13 analytes listed in Table 1, the method EMON-SM-05-061 (CDFA, 2025) uses a triple quadrupole mass spectrometer in the multiple reaction monitoring (MRM) mode for quantification. Monitoring for each target analyte occurs in a window surrounding the compound’s retention time following chromatographic separation. Retention times are confirmed via certified reference standards. The first quadrupole in the mass spectrometer filters precursor ions with selected mass-to-charge ratios corresponding to the analytes’ molecular ion. Each precursor ion is then fragmented in the next stage. Finally, the third quadrupole in the mass spectrometer filters for characteristic fragment ions of the target analytes. Fragment ions are used for quantification and confirmation of each species. Therefore, this method uses four stepwise factors to eliminate possible interferences for these pesticides: chromatographic retention times, molecular ion masses, specific product ion masses, and product ion ratios.

NOTE: Orthosulfamuron and triclopyr are considered marginal compounds due to recovery issues observed during method validation. Nevertheless, their identification in groundwater using method EMON-SM-05-061 (CDFA, 2025) is highly specific and meets the criteria for unequivocal identification.

As specifically stated in method EMON-SM-05-061 (CDFA, 2025), the presence of azoxystrobin acid, bensulfuron-methyl, bispyribac sodium, clomazone, halosulfuron methyl, MCPA, molinate, orthosulfamuron, penoxsulam, propanil, propiconazole, thiobencarb, and triclopyr in groundwater is confirmed by:

1. The retention time of the analyte is within ± 0.1 minutes of each analyte within the same sequence.
2. The relative abundances of structurally significant ions used for confirmation are within ± 30% when compared to a standard injected during the same run.

Identification for these 13 analytes in groundwater by method EMON-SM-05-061 (CDFA, 2025) is highly specific and qualifies as an unequivocal method. Therefore, confirmation by a second laboratory or use of a second method is not necessary for groundwater samples analyzed for these pesticides by this method.

APPROVED: *Original Signed by* Date: *7/31/25*
Joy Dias
Environmental Program Manager I

APPROVED: *Original Signed by* Date: *7/31/25*
Maziar Kandelous
Environmental Program Manager II (Acting)

REFERENCES

Aggarwal, V. 2012. Memorandum to Lisa Ross, Ph.D. Evaluating analytical methods for compliance with the Pesticide Contamination Prevention Act requirements. Available at: https://www.cdpr.ca.gov/wp-content/uploads/2024/11/pcpa_requirements_analytical_methods_compliance.pdf (accessed June 10, 2025).

CDFA. 2025. EMON-SM-05-061. Determination of Selected Rice Herbicides in Groundwater. California Department of Food and Agriculture, Sacramento, California.