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MEMORANDUM

TO: Joy Dias
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Original Signed by 7/23/25

DATE: July 22, 2025

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-062 REVISION 7 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-05-062 REVISION 7 (CDFA, 2025) is unequivocal according to the Pesticide Contamination Prevention Act.

PURPOSE

Determine if the analytical method, EMON-SM-05-062 REVISION 7 (CDFA, 2025), for atrazine, bromacil, diuron, hexazinone, metribuzin, norflurazon, prometon, prometryn, simazine, desethylatrazine, norflurazon desmethyl, desisopropylatrazine, diaminochlorotriazine, tebuthiuron, clothianidin, and simazine-2-hydroxy 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-05-062 REVISION 7 (CDFA, 2025) uses a liquid chromatography-triple quadrupole mass spectrometry (LC/MS/MS) system for the detection of the 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 passed through a mixed-mode cation exchange (MCX) cartridge (Waters Oasis® MCX 6 cc, 150 mg). The analytes (Table 1) are then eluted with 7-8% ammonium hydroxide in methanol. The eluant is then concentrated to less than 1.0 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen and then brought up to a final volume of 2.0 mL with reconstitution reagent (1:1 (v:v) methanol/water). The extract is then analyzed by LC/MS/MS. Propazine is used as a surrogate to verify extraction efficiency.

Table 1. Pesticides determined by LC/MS/MS in CDFA Method EMON-SM-05-062 REVISION 7.

Atrazine	Metribuzin
Bromacil	Norflurazon
Clothianidin	Norflurazon desmethyl
Desethylatrazine	Prometon
Desisopropylatrazine	Prometryn
Diaminochlorotriazine	Simazine
Diuron	Simazine-2-hydroxy
Hexazinone	Tebuthiuron

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 analytes listed in Table 1, the method EMON-SM-05-062 REVISION 7 (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: The lower control limit (LCL) for hexazinone during method validation was below 50%. Compounds with LCLs under 50% are classified as marginal. However, hexazinone's identification in groundwater using method EMON-SM-05-062 REVISION 7 (CDFA, 2025) is highly specific and meets the criteria for unequivocal identification.

As specifically stated in method EMON-SM-05-062 REVISION 7 (CDFA, 2025), the presence of atrazine, bromacil, diuron, hexazinone, metribuzin, norflurazon, prometon, prometryn, simazine, desethylatrazine, norflurazon desmethyl, desisopropylatrazine, diaminochlorotriazine, tebuthiuron, clothianidin, and simazine-2-hydroxy 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 $\pm 30\%$ when compared to a standard injected during the same run.

Identification for these analytes in groundwater by method EMON-SM-05-062 REVISION 7 (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 and degradates by this method.

APPROVED: *Original Signed by*
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Environmental Program Manager I

Date: *7/23/25*

APPROVED: *Original Signed by*
Maziar Kandelous
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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-05-062 REVISION 7. Determination of Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Desethylatrazine, Norflurazon Desmethyl, Desisopropylatrazine, Diaminochlorotriazine, Tebuthiuron, Clothianidin, and Simazine-2-hydroxy in Groundwater by Liquid Chromatography Triple Quadrupole Mass Spectrometry. California Department of Food and Agriculture, Sacramento, California.