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DATE: July 28, 2025

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-060 (DRAFT) AS UNEQUIVOCAL ACCORDING TO THE PESTICIDE CONTAMINATION PREVENTION ACT – **INTERIM MEMORANDUM**

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 draft version of the analytical method EMON-SM-05-060 (CDFA, 2025) for 59 pesticides 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-05-060 (CDFA, 2025) uses either a liquid chromatography coupled to a tandem mass spectrometer (LC/MS/MS) system, or a gas chromatography coupled to a tandem mass spectrometer

(GC/MS/MS) system for the detection of 59 pesticides in groundwater. LC/MS/MS is used for the determination of 45 pesticides (Table 1), while GC/MS/MS is used for the detection of 14 pesticides (Table 2). Prior to injection of a sample into the LC/MS/MS or GC/MS/MS apparatus, the analytes are extracted from the groundwater sample (250 g) with methylene chloride. Two surrogates; atrazine-d_5 and imidacloprid-d_4 are used to verify extraction efficiency.

Table 1. Pesticides determined by LC/MS/MS in CDFA Method EMON-SM-05-060.

AIBA	Isoxaben
Atrazine	Linuron
Atrazine-d_5 (surrogate)	Mefenoxam
Azinphos-methyl	Methiocarb
Azoxystrobin	Methomyl
Bensulide	Methoxyfenozide
Bromacil	S-Metolachlor
Carbaryl	Metribuzin
Carbofuran	Myclobutanil
Chlorantraniliprole	Napropamide
Cyprodinil	Norflurazon
Diazinon	Oryzalin
Dimethenamide	Piperonyl Butoxide
Dimethoate	Prometon
Diuron	Propanil
Ethofumesate	Propiconazole
Ethoprophos	Pyraclostrobin
Fenamiphos	Simazine
Fludioxonil	Tebuthiuron
Flupyradifurone	Thiamethoxam
Flutriafol	Thiobencarb
Imidacloprid	Uniconazole
Imidacloprid-d_4 (surrogate)	

Table 2. Pesticides determined by GC/MS/MS in CDFA Method EMON-SM-05-060.

Alachlor	Fonofos
Benfluralin	Malathion
Clomazone	Parathion Ethyl
Dichlobenil	Parathion Methyl
Dichloran	Phorate
Disulfoton	Prometryn
EPTC	Triallate

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 above mentioned 59 pesticides listed in Tables 1 and 2, the method EMON-SM-05-060 (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 AIBA, dichlobenil, disulfoton, ethoprophos, EPTC, flupyradifrone, phorate, and propiconazole during method validation was below 50%. Compounds with LCLs under 50% are classified as marginal. However, identification of these compounds in groundwater using method EMON-SM-05-060 (CDFA, 2025) is highly specific and meets the criteria for unequivocal identification.

As specifically stated in method EMON-SM-05-060 (CDFA, 2025), the presence of 59 pesticides in groundwater are 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 59 pesticides in groundwater by method EMON-SM-05-060 (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 59 pesticides by this method.

APPROVED: *Original Signed by* Date: *7/31/25*
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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-05-060. Determination of 59 Pesticides in 250 mL Groundwater Samples by Liquid Chromatography Tandem Mass Spectrometry and Gas Chromatography Tandem Mass Spectrometry. California Department of Food and Agriculture, Sacramento, California.