



MEMORANDUM

TO: Joy Dias
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Original Signed by 5/23/23

DATE: May 16, 2023

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-034A REVISION 4 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 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-05-034A Revision 4 (CDFA, 2023) is unequivocal according to the Pesticide Contamination Prevention Act.

PURPOSE

Determine if the analytical method (EMON-SM-05-034A Revision 4) (CDFA, 2023) for S-metolachlor, metolachlor ethanesulfonic acid, metolachlor oxanilic acid, deschloro metolachlor, and hydroxy metolachlor 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-05-034A Revision 4 (CDFA, 2023) uses a liquid chromatography tandem mass spectrometry (LC/MS/MS) system for the detection of S-metolachlor, metolachlor ethanesulfonic acid, metolachlor oxanilic acid, deschloro metolachlor, and hydroxy metolachlor in groundwater (Table 1). Prior to injection of a sample

into the LC/MS/MS, a measured volume of groundwater sample (50 mL) is passed through an Oasis HLB solid phase extraction (SPE) cartridge (Waters, Oasis HLB 0.2 g 6cc). The analytes (Table 1) are then eluted with methanol. The eluant is then evaporated in a water bath at 40 ± 2 °C with a gentle stream of nitrogen to approximately 0.4 mL. The volume of extract is adjusted to 0.5 mL with methanol, and then brought up to a final volume of 1.0 mL with water. The extract is then analyzed by LC/MS/MS.

Table 1. Pesticides determined by LC/MS/MS in CDFA Method EMON-SM-05-034A Revision 4.

S-Metolachlor	Deschloro Metolachlor
Metolachlor Ethanesulfonic Acid (ESA)	Hydroxy Metolachlor
Metolachlor Oxanilic Acid (OXA)	

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-05-034A Revision 4 (CDFA, 2023) sets the first quadrupole in the mass spectrometer to reject all species with mass/charge values that do not correspond to the analyte’s molecular ion eluting at that analyte’s particular retention time. Each molecular ion is then fragmented in the next stage, and finally the third quadrupole in the mass spectrometer quantifies the pesticides based on either one or two characteristic fragments. Therefore, this method uses three stepwise factors to eliminate possible interferences for these pesticides: chromatographic retention times, molecular ion masses, and specific product ion masses.

As specifically stated in method EMON-SM-05-034A Revision 4 (CDFA, 2023), the presence of S-metolachlor, metolachlor ethanesulfonic acid, metolachlor oxanilic acid, deschloro metolachlor, and hydroxy metolachlor in groundwater is confirmed by:

1. The retention time of the analyte within ± 0.1 minute of each analyte of that of the standards.
2. The relative abundance or ratio of selective ions within $\pm 30\%$ when compared to a standard injected during the same run.

Identification for these analytes in groundwater by method EMON-SM-05-034A Revision 4 (CDFA, 2023) is highly specific and qualifies as an unequivocal method. Therefore, confirmation

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by a second laboratory or use of a second method is not necessary for groundwater samples analyzed for S-metolachlor and degradates by this method.

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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/docs/emon/grndwtr/polprocd/pcpa_requirements_analytical_methods_compliance.pdf (accessed April 27, 2023).
- CDFA. 2023. EMON-SM-05-034A Revision 4. Analysis of S-Metolachlor, Metolachlor Ethanesulfonic Acid, Metolachlor Oxanilic Acid, Deschloro Metolachlor, and Hydroxy Metolachlor in Groundwater. California Department of Food and Agriculture, Sacramento, California.