



MEMORANDUM

TO: Carissa Ganapathy
Senior Environmental Scientist (Supervisory)
Environmental Monitoring Branch

FROM: Vaneet Aggarwal, Ph.D.
Environmental Scientist
916-445-3870

Original Signed by 7/13/22

DATE: July 12, 2022

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-034A REVISION 2 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 is considered detected in groundwater, and thus subject to formal review as specified. FAC subsection 13149(d) allows a finding of a pesticide 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 2 (CDFA, 2022) is unequivocal according to the Pesticide Contamination Prevention Act.

PURPOSE

Determine if the analytical method (EMON-SM-05-034A revision 2) (CDFA, 2022) for S-metolachlor, metolachlor ESA, and metolachlor OXA in well water used by the California Department of Food and Agriculture (CDFA) meets the definition of an unequivocal method.

DISCUSSION AND RECOMMENDATION

The CDFCA Center for Analytical Chemistry method EMON-SM-05-034A revision 2 (CDFCA, 2022) uses a liquid chromatography coupled to a tandem quadrupole mass spectrometer (LC/MS/MS) system for the detection of S-metolachlor, metolachlor ESA, and metolachlor OXA in well water. Prior to injection of a sample into the LC/MS/MS, a measured volume of groundwater sample (50 mL) is passed through a solid phase extraction cartridge (Waters Oasis

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HLB 0.2 g 6 cc). The cartridge is rinsed with water and the analytes are then eluted with methanol. The methanol is evaporated at 45 °C with a gentle stream of nitrogen to ~ 0.4 mL. The volume of the extract is adjusted to 0.5 mL with water, and then brought up to a final volume of 1.0 mL with methanol. The extract is then analyzed by LC/MS/MS.

A method is considered “unequivocal” based on (a) matching retention time of the certified reference standard, (b) presence of the precursor ion at the retention time, and/or (c) presence of one or more characteristic product ions (Aggarwal, 2012). In method EMON-SM-05-034A revision 2 (CDFA, 2022) for S-metolachlor, metolachlor ESA, and metolachlor OXA, the first quadrupole in the mass spectrometer is set 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 2 (CDFA, 2022), the presence of S-metolachlor, metolachlor ESA, and metolachlor OXA in well water is confirmed by:

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

Analysis of S-metolachlor, metolachlor ESA, and metolachlor OXA by method EMON-SM-05-034A revision 2 (CDFA, 2022) is highly specific and qualifies as an unequivocal method. Therefore, analysis by a second laboratory or a second method is not necessary for well water samples analyzed for S-metolachlor, metolachlor ESA, and metolachlor OXA by this method.

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APPROVED: Original Signed by Date: *7/13/22*
Carissa Ganapathy
Senior Environmental Scientist (Supervisory)

APPROVED: Original Signed by Date: *7/13/22*
Joy Dias
Environmental Program Manager I
Acting Environmental Program Manager II

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 July 12, 2022).
- CDFA. 2022. EMON-SM-05-034A Rev 2. Analysis of S-Metolachlor, Metolachlor ESA, and Metolachlor OXA in Well Water. California Department of Food and Agriculture, Sacramento, California.