



Julie Henderson
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MEMORANDUM

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

DATE: May 16, 2023

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-051 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-05-051 (CDFA, 2023) is unequivocal according to the Pesticide Contamination Prevention Act.

PURPOSE

Determine if the analytical method (EMON-SM-05-051) (CDFA, 2023) for metribuzin, metribuzin desamino, metribuzin diketo, and metribuzin desaminodiketo 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-05-051 (CDFA, 2023) uses a liquid chromatography Electro Spray Ionization Mass Spectrometry (LC/ESI/MS/MS) system for the detection of metribuzin, metribuzin desamino, metribuzin diketo, and metribuzin desaminodiketo in groundwater (Table 1). Prior to injection of a sample into the LC/ESI/MS/MS, a measured volume of groundwater sample (100 mL) is passed through an

MCX cartridge (Waters Oasis MCX 6 cc, 150 mg). The analytes (Table 1) are then eluted with ammonium hydroxide in methanol. The eluant is evaporated to dryness in water bath at 38 ± 2 °C under a gentle stream of nitrogen, and then brought up to a final volume of 1.0 mL with 1:1, acetonitrile/water. The extract is then analyzed by LC/ESI/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-05-051.

Metribuzin	Metribuzin Desamino
Metribuzin Diketo	Metribuzin Desaminodiketo

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-05-051 (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-05-051 (CDFA, 2023), the presence of metribuzin, metribuzin desamino, metribuzin diketo, and metribuzin desaminodiketo in groundwater is confirmed by:

1. The retention time of the analyte within ± 0.1 minute of each analyte in the standards within the same sequence.
2. The relative abundance of structurally significant ions used for confirmation within $\pm 30\%$ when compared to a standard injected during the same run.

Identification for these analytes in groundwater by method EMON-SM-05-051 (CDFA, 2023) 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 metribuzin 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 24, 2023).
- CDFA. 2023. EMON-SM-05-051. Determination of Metribuzin, Metribuzin Desamino, Metribuzin Diketo, and Metribuzin Desaminodiketo in Groundwater by Liquid Chromatography Electro Spray Ionization Mass Spectrometry. California Department of Food and Agriculture, Sacramento, California.