Department of Pesticide Regulation

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MEMORANDUM

TO: Joy Dias *Original Signed by 3/6/24*
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DATE: February 27, 2024

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-044 REVISION 1 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-05-044 Revision 1 (CDFA, 2023) is unequivocal according to the Pesticide Contamination Prevention Act.

PURPOSE

Determine if the analytical method EMON-SM-05-044 Revision 1 (CDFA, 2023) for azoxystrobin acid, bensulfuron-methyl, bispyribac sodium, clomazone, halosulfuron methyl, 2-methyl-4-chlorophenoxyacetic acid (MCPA), molinate, orthosulfamuron, penoxsulam, propanil, propiconazole, thiobencarb, and triclopyr 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-05-044 Revision 1 (CDFA, 2023) uses a liquid chromatograph coupled to a tandem mass spectrometer (LC/MS/MS) for the

detection of azoxystrobin acid, bensulfuron-methyl, bispyribac sodium, clomazone, halosulfuron methyl, MCPA, molinate, orthosulfamuron, penoxsulam, propanil, propiconazole, thiobencarb, and triclopyr in groundwater (Table 1). Prior to injection of a sample into the LC/MS/MS, a measured volume of groundwater sample (500 mL) is acidified with 3N hydrochloric acid (HCl) and passed through a solid phase extraction cartridge (Water's Oasis® HLB 6 cc). The analytes are then eluted with 5.0 mL of acetonitrile/methanol (50/50 v/v) solution and the eluant is concentrated to ~ 1.8 mL under a gentle stream of nitrogen in a water bath. The eluant is then brought up to a final volume of 2.0 mL with acetonitrile/methanol (50/50 v/v) solution. The extract is then analyzed by LC/MS/MS. Two surrogates; 2,4,5-T and simazine-d_{10} are used to verify extraction efficiency.

Table 1. Pesticides determined by LC/MS/MS in CDFA Method EMON-SM-05-044 Revision 1.

Azoxystrobin acid	Orthosulfamuron
Bensulfuron-methyl	Penoxsulam
Bispyribac sodium	Propanil
Clomazone	Propiconazole
Halosulfuron methyl	Thiobencarb
MCPA	Triclopyr
Molinate	

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-05-044 Revision 1 (CDFA, 2023) sets the first quadrupole in the mass spectrometer to filter out all species with mass-to-charge value that does 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-05-044 Revision 1 (CDFA, 2023), the presence of azoxystrobin acid, bensulfuron-methyl, bispyribac sodium, clomazone, halosulfuron methyl, MCPA, molinate, orthosulfamuron, penoxsulam, propanil, propiconazole, thiobencarb, and triclopyr in groundwater is confirmed by:

1. The retention time of the analyte shall not vary from standards more than ± 0.1 minute.
2. The relative abundance of structurally significant ions used for confirmation must be within ± 30% relative when compared to a standard injected during the same run.

Identification for these analytes in groundwater by method EMON-SM-05-044 Revision 1 (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 these pesticides by this method.

APPROVED: *Original Signed by* Date: *3/6/24*
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Date: *3/6/24*
Minh Pham
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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 February 27, 2024).

CDFA. 2023. EMON-SM-05-044 Revision 1. Determination of Selected Rice Herbicides in Groundwater. California Department of Food and Agriculture, Sacramento, California.