



MEMORANDUM

TO: Carissa Ganapathy
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Environmental Monitoring Branch

FROM: Vaneet Aggarwal, Ph.D. *Original Signed by Carissa Ganapathy for 4/15/20*
Environmental Scientist
916-445-3870

DATE: April 9, 2020

SUBJECT: THE QUALIFICATION OF METHOD EMON-SM-05-044 AS UNEQUIVOCAL
ACCORDING TO CRITERIA IN 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 which may be used for drinking water supplies. FAC section 13149 specifies the conditions under which a pesticide is considered “found” in groundwater or soil, and thus subject to formal review as specified. FAC subsection 13149(d) allows a finding of a pesticide in groundwater or soil to be based on a single analytical method conducted by a single analytical laboratory, only if the analytical method provides unequivocal identification of a chemical. The criteria and discussion of DPR’s process for qualifying methods that provide unequivocal identification of a chemical are 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 criteria. This qualification memo serves to establish if the method EMON-SM-05-044 meets those criteria.

PURPOSE

Determine if the analytical method (EMON-SM-05-044) for Bensulfuron-methyl, Bispyribac sodium, Clomazone, Halosulfuron methyl, 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 uses a Liquid Chromatography coupled to a Linear Ion Trap Quadrupole (LC/MS/MS) for the detection of Bensulfuron-methyl, Bispyribac sodium, Clomazone, Halosulfuron methyl, MCPA, Molinate, Orthosulfamuron, Penoxsulam, Propanil, Propiconazole, Thiobencarb, and Triclopyr in

groundwater. Prior to the injection of a sample into the LC/MS/MS, a measured volume of groundwater sample (500 mL) is acidified with 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) solution and the eluant is concentrated to ~ 1.8 mL in a water bath. The eluant is then brought up to a final volume of 2.0 mL with acetonitrile/methanol (50:50) solution. 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-05-044, 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 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, the following criteria are used to confirm the presence of Bensulfuron-methyl, Bispyribac sodium, Clomazone, Halosulfuron methyl, MCPA, Molinate, Orthosulfamuron, Penoxsulam, Propanil, Propiconazole, Thiobencarb, and Triclopyr in groundwater:

1. For positive results, the retention time shall not vary from standards by more than ± 0.1 minute.
2. Presence of both qualification and quantification ion.
3. The relative abundance of confirmation ions must be within $\pm 30\%$ when compared to the relative abundance of the same ions for a standard injected during the same run.

Analysis of Bensulfuron-methyl, Bispyribac sodium, Clomazone, Halosulfuron methyl, MCPA, Molinate, Orthosulfamuron, Penoxsulam, Propanil, Propiconazole, Thiobencarb, and Triclopyr by method EMON-SM-05-044 is highly specific and qualifies for unequivocal detection designation. Therefore, analysis by a second laboratory or a second method is not necessary for groundwater samples analyzed for Bensulfuron-methyl, Bispyribac sodium, Clomazone, Halosulfuron methyl, MCPA, Molinate, Orthosulfamuron, Penoxsulam, Propanil, Propiconazole, Thiobencarb, and Triclopyr using this method.

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April 9, 2020
Page 3

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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 March 24, 2020).