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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 EM-SM-05-053 AS UNEQUIVOCAL  
ACCORDING TO THE PESTICIDE CONTAMINATION PREVENTION ACT

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**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 EM-SM-05-053 (CDFA, 2022) is unequivocal according to the Pesticide Contamination Prevention Act.

**PURPOSE**

Determine if the analytical method EM-SM-05-053 (CDFA, 2022) for aminopyralid in groundwater 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 EM-SM-05-053 (CDFCA, 2022) uses a liquid chromatography-triple quadrupole mass spectroscopy (LC/MS/MS) system for the detection of aminopyralid in groundwater. Prior to injection of a sample into the LC/MS/MS, a measured volume of groundwater sample (10 mL) is passed through a 0.45 µm Nylon filter. The filter is rinsed with acetonitrile. The extract is then analyzed by LC/MS/MS. 5-amino-2-chlorobenzoic

acid is used as an internal standard and acetonitrile is used as a washing solution to normalize response data for potential matrix effects in environmental samples with matrix interferences.

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).

In method EM-SM-05-053 (CDFA, 2022) for aminopyralid, 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 EM-SM-05-053 (CDFA, 2022), the presence of aminopyralid in groundwater is confirmed by:

1. The retention time of the analyte within  $\pm 0.1$  minute of that of the standard.
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 of aminopyralid in groundwater by method EM-SM-05-053 (CDFA, 2022) 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 aminopyralid 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](https://www.cdpr.ca.gov/docs/emon/grndwtr/polprocd/pcpa_requirements_analytical_methods_compliance.pdf) (accessed April 24, 2023).
- CDFA. 2022. EM-SM-05-053. Analysis of Aminopyralid in Groundwater by Liquid Chromatography Triple Quadrupole Mass Spectrometry. California Department of Food and Agriculture, Sacramento, California.