



## MEMORANDUM

TO: Carissa Ganapathy  
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Environmental Monitoring Branch

FROM: Vaneet Aggarwal, Ph.D. *Original Signed by 7/16/20*  
Environmental Scientist  
916-445-3870

DATE: July 16, 2020

SUBJECT: THE QUALIFICATION OF METHOD EM 62.9 AS UNEQUIVOCAL  
ACCORDING TO CRITERIA IN 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 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 EM 62.9 meets those criteria.

### PURPOSE

Determine if the analytical method (EM 62.9) for Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotriazine (DACT), Desmethyl-Norflurazon, Tebuthiuron and the metabolites Tebuthiuron-104, Tebuthiuron-106, Tebuthiuron-107 and Tebuthiuron-108 in groundwater used by the California Department of Food and Agriculture (CDFA) meets the definition of an unequivocal method. Please note that the original method included tebuthiuron and the metabolites. Tebuthiuron is also analyzed utilizing another method (EMON-SM-05-032). DPR no longer requests analysis of Tebuthiuron metabolites, consequently CDFA did not update the Method Detection Limits (MDL) and Reporting Limit (RL) for Tebuthiuron metabolites.

## DISCUSSION AND RECOMMENDATION

The CDFA Center for Analytical Chemistry method EM 62.9 uses a Liquid Chromatography coupled to a Linear Ion Trap Quadrupole (LC/MS/MS) for the detection of Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotriazine (DACT), Desmethyl-Norflurazon, and Tebuthiuron 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 (Waters Oasis<sup>®</sup> MCX 6 cc). The analytes are then eluted with 15.0 mL of 5% ammonium hydroxide in methanol and the eluant is concentrated to ~10 mL in a water bath. The eluant is then filtered through a 0.2 µm Acrodisc, followed by concentrating the eluant to ~0.5 mL in a water bath, and then bringing up to a final volume of 1.0 mL with 1:3 methanol/water. 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 EM 62.9, 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 EM 62.9, the following criteria are used to confirm the presence of Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotriazine (DACT), Desmethyl-Norflurazon, and Tebuthiuron in groundwater:

1. The retention time of the analyte must match within  $\pm 0.1$  minute of the analyte in the standards within the same sequence.
2. Presence of both precursor and product ion. The relative abundances of structurally significant ions used for confirmation must be within  $\pm 30\%$  relative when compared to a standard injected during the same run.

Analysis of Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotriazine (DACT), Desmethyl-Norflurazon, and Tebuthiuron by method EM 62.9 is highly specific and qualifies for unequivocal detection designation. Therefore, analysis by a second

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laboratory or a second method is not necessary for groundwater samples analyzed for Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotriazine (DACT), Desmethyl-Norflurazon, and Tebuthiuron using 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 July 09, 2020).