Department of Pesticide Regulation

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SUBJECT: DETERMINATION IF CALIFORNIA DEPARTMENT OF FISH AND WILDLIFE'S SELECTED RICE HERBICIDES METHOD (WPCL-LC-009) MEETS THE "UNEQUIVOCAL DETECTION" CRITERIA

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 ground water which may be used for drinking water supplies. FAC section 13149 specifies the conditions under which a pesticide is considered "found" in ground water or soil, and thus subject to formal review as specified. FAC subsection 13149(d) allows a finding of a pesticide in ground water or soil to be based on a single analytical method conducted by a single analytical laboratory, if the analytical method provides unequivocal identification of a chemical. Criteria to identify methods providing unequivocal identification of a chemical are included in a DPR memo entitled "Evaluating analytical methods for compliance with the Pesticide Contamination Prevention Act Requirements" (Aggarwal, 2012).

ISSUE

Does the analytical method for selected rice herbicides used by the California Department of Fish and Wildlife (CDFW) meet the definition of an unequivocal detection method?

DISCUSSION AND RECOMMENDATION

CDFW Water Pollution Control Laboratory method (WPCL-LC-009) uses a Liquid Chromatography coupled to triple quadrupole mass spectrometry (LC/MS/MS) system for the detection of selected rice herbicides (Penoxsulam, Orthosulfamuron, Clomazone, Propanil, Bensulfuron-methyl, Molinate, Bispyribac-sodium, Halosulfuron-methyl, Propiconazole, Thiobencarb, and Triclopyr). Prior to injection of sample into the LC/MS/MS apparatus, the well water samples are extracted by passing the sample through a solid phase extraction cartridge. Well water samples generally contain a minimal amount of background/matrix interference which facilitates the goal of unequivocal detection.

In CDFW method WPCL-LC-009 for selected rice herbicides (Penoxsulam, Orthosulfamuron, Clomazone, Propanil, Bensulfuron-methyl, Molinate, Bispyribac-sodium, Halosulfuron-methyl, Propiconazole, Thiobencarb, and Triclopyr) analysis, the first 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 final mass spectrometer quantifies the pesticides based on either one or two characteristic fragments. Three stepwise factors are used to eliminate possible interferences for Penoxsulam, Orthosulfamuron, Clomazone, Propanil, Bensulfuron-methyl, Molinate, Bispyribac-sodium, Halosulfuron-methyl, Propiconazole, Thiobencarb, and Triclopyr: chromatographic retention times, molecular ion masses and specific daughter ion masses.

In CDFW method WPCL-LC-009, the following criteria are used to confirm the presence of Penoxsulam, Orthosulfamuron, Clomazone, Propanil, Bensulfuron-methyl, Molinate, Bispyribac-sodium, Halosulfuron-methyl, Propiconazole, Thiobencarb, and Triclopyr:

1. Each set of samples will have a method blank and a spiked matrix sample.
2. Target compounds must be less than the reporting limit or project requirements, whichever is more stringent.
3. The recoveries of the matrix spikes shall be within the control limits.
4. Each analyte has a precursor/parent ion and corresponding product/daughter ion that needs to be present in order to quantify that analyte.

Analysis of the Penoxsulam, Orthosulfamuron, Clomazone, Propanil, Bensulfuron-methyl, Molinate, Bispyribac-sodium, Halosulfuron-methyl, Propiconazole, Thiobencarb, and Triclopyr by method WPCL-LC-009 is highly specific and qualifies for **unequivocally detection** designation. Therefore, analysis by a second laboratory or a second method is not necessary for well water samples analyzed for Penoxsulam, Orthosulfamuron, Clomazone, Propanil, Bensulfuron-methyl, Molinate, Bispyribac-sodium, Halosulfuron-methyl, Propiconazole, Thiobencarb, and Triclopyr by this method.

Results indicate that up to 70% of the orthosulfamuron may have been lost within 10 days of extraction due to instability of orthosulfamuron stored at 4^{o} C. Additional studies are underway to investigate optimal orthosulfamuron storage conditions. Until these studies are completed, orthosulfamuron values will be reported as estimated values. However, this does not impact the unequivocal identification of orthosulfamuron by WPCL-LC-009 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. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/2391_ross.pdf (accessed 06 November 2013).