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SUBJECT: ASSESSMENT OF THE NEED FOR AND VALUE OF FORTIFIED FIELD SPIKES AS PART OF AMBIENT AIR MONITORING STUDIES CONDUCTED BY THE DEPARTMENT OF PESTICIDE REGULATION’S AIR PROGRAM

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The Department of Pesticide Regulation (DPR) has conducted ambient air monitoring studies since the 1980s. The following types of quality control (QC) samples or studies are conducted as part of DPR’s air monitoring study procedures:

- **Trapping efficiency study**
  - Conducted to determine appropriate sample media, duration of sampling, and the volume of air needed. This study helps determine the ability to trap the pesticide of interest in the selected sampling media and provides confidence in the resulting concentrations for a study.

- **Storage stability study**
  - Conducted to determine the stability of collected residues during sample storage prior to their analysis. A storage stability study may validate the residue’s rate of decomposition in a representative matrix.

- **Laboratory blank**
  - An analyte-free matrix sample that is used along with prepared standards to calibrate the instrument and to evaluate instrument contamination.

- **Laboratory fortified matrix spike**
  - A laboratory sample to which a known quantity of pesticide has been added. It is used to assess whether the sample matrix contributes bias to the analytical results and helps evaluate analyte recovery in a sample. This sample is not exposed to field conditions.
- Field blank
  - A sample that contains no pesticide residue. It is used to assess potential field and laboratory contamination issues.

- Co-located duplicate
  - A sample that is collected adjacent to the primary air sample under the same conditions. It is used to assess for field measurement precision and analytical measurements.

- Fortified field spike
  - A sample to which a known quantity of pesticide has been added and are placed on air sampling equipment to sample air under the same conditions as the primary air sample. This sample is used to assess recoveries under field conditions.

While trapping efficiency, storage stability, laboratory blanks, laboratory fortified matrix spikes, field blanks, and co-located duplicates are a common practice in ambient air monitoring studies, fortified field spikes are not. To our knowledge, DPR is among the few organizations that actually collects fortified field spikes as part of ambient air monitoring sampling. The other organizations that have collect them; only do so at DPRs request or following DPR’s lead:

- California Air Resources Board (CARB) only collects fortified field spikes “as a special request from DPR and are not a part of the OLS standard operating procedures nor of US EPA’s Method TO-15.” (CARB, 2018).

- Washington State Department of Health’s (WSDH) Pesticide Program (WSDH) collected them for their pesticide air monitoring study following the approach “as defined by the California Department of Pesticide Regulation” (WSDH, 2009).

Some reasons why fortified field spike samples are not normally collected as part of ambient air monitoring studies are due to: [1] the lack of commercially available pesticide gas standards; [2] difficulty of accurately introducing a known amount of an airborne chemical into the sampling media in a way that mimics the manner in which the chemical is collected in the field; and [3] lack of meaningful data that can be gathered from fortified field spike results.

Several reasons exists as to why fortified field spikes recoveries may fall outside of the acceptable criteria but may not be a result of collection or analytical issues. These reasons are listed below:
1. Different spiked amount
   a. Actual amount spiked may be lower or higher than the amount reported.

2. Volatilization or degradation
   a. The concentration of the spiked pesticide may decrease through volatilization or
degradation during either sample preparation or transport.

3. Low spiked amounts
   a. Spike amount is too low compared to ambient air concentration levels leading to
erroneous spike recoveries due to inherent sampling and analysis variation.
   i. For example, if 10 micrograms of a pesticide are added to the field
fortified spike sample, but the co-located field sample collected during
sampling contains 100 micrograms, normal variation can cause an
erroneously low or high spike recovery.
   b. Estimating an appropriate spike amount is problematic since the ambient pesticide
concentration is unknown.

4. Humidity effects on recoveries
   a. Recoveries of fumigants are particularly sensitive to extreme humidity levels (low
or high). Biermann and Barry (1999) showed very low recoveries of methyl
bromide from charcoal tubes at low humidity. CARB showed similar results with
recoveries of methyl bromide from canisters under low humidity conditions.
CARB has also shown that under high humidity levels, recovery of methyl
bromide from air canisters can be very low.
   b. Preparing spiked samples at ambient humidity levels is problematic.

5. Spiking delivery method
   a. Delivery method may differ from the conditions under which the pesticide is
collected in the field.
   b. Biermann and Barry (1999) determined that any fumigant-spiking method must
mimic the conditions under which the fumigant is collected in the field in order to
provide any confidence in the obtained results.

DPR began to incorporate fortified field spikes into its ambient air monitoring studies in the mid-
1990s; however, questions about the validity, value, and significance of spike recovery results
emerged soon thereafter (Biermann and Barry, 1999). Most of these questions are due to the
spiking delivery method utilized. The method to introduce a pesticide into the sampling media, in
the absence of pesticide gas standards, has been by injecting a solvent solution that contains the
dissolved pesticide into the sampling media. Both the California Department of Food and
Agriculture’s (CDFA) Center of Analytical Chemistry and the CARB’s Organics Laboratory
Section currently prepare fortified field spikes by dissolving pesticides in a solvent mixture and
injecting the spiking solution onto the sampling media. This spiking process differs from environmental conditions and may inadvertently affect the results since ambient pesticides are not dissolved in a solvent. This is especially true for fumigants spiked as liquid solutions, since the fumigants exist as a gaseous phase in the environment. Additionally, the spiking solution is added as a single liquid injection instead of as a steady, low-level 24-hour concentration as it would be in the field, which further differentiates fortified field spike samples from field collected ambient air samples.

Recent fortified field spike sample recoveries from DPR’s and ARB’s pesticide air monitoring studies have seen recovery percent fluctuations ranging from 0% to 1,120%. Unfortunately, being able to identify the root cause of these extreme low or high recoveries is not possible and although in the past DPR has adjusted the results of the field samples when spike recoveries were outside an acceptable range, this was only done when the reasons for low recovery could be clearly identified and quantified. However, for the reasons described above, the fortified field spike recoveries may not accurately indicate the performance of the sampling and laboratory methods; therefore, being able to identify and quantify the cause of the low recoveries is not possible.

Recent evaluations into low recoveries of methyl bromide and methyl isothiocyanate fortified field spikes conducted by outside agencies indicate problems with the spikes and the spiking process, rather than a problem with the collected field samples (CARB 2018; CDFA 2018a; CDFA 2018b; Collins 2018). Specific conclusions or comments made by these agencies include:

- **CARB:**
  - “Our conclusion is that the low matrix spike recoveries for samples analyzed on Agilent F are due to the addition of water in the laboratory. This impacted only the bromomethane matrix spike results which should be invalidated. The data for all unspiked field samples analyzed in 2017 are valid.” (CARB 2018)

- **USEPA Region 9:**
  - “Given the field spike results, it is not appropriate to suggest that actual concentrations in ambient air might have been either higher or lower than measured. Other acceptable QC results should be highlighted as reasons to accept the field results.” (Collins 2018)

- **CDFA:**
  - “Using liquid solution spiking methodology to measure system performance may not be suitable as it can be influenced by other variable environmental conditions that may contribute to low spike recoveries. This is not an effective way to evaluate the lab proficiency, which is an important goal of blind matrix spikes
studies and most importantly the entire measurement system without ability to isolate analyte loss at each step.” (CDFA 2018b)

Recommendation

Although fortified field spike samples provide some additional information on recovery from the sampling matrix, the value of these samples, as currently prepared and handled, in assessing any QC aspect of the air monitoring studies conducted by DPR’s Air Program is debatable. Results from trapping efficiency studies, storage stability studies, as well as those from laboratory blanks, laboratory fortified field spikable field spikes, field blanks, and co-located samples provide greater verifiable information and give DPR confidence in the analytical method and resulting air concentrations. Therefore, for the reasons mentioned above, we recommend terminating the collection of fortified field spikes as part of air monitoring studies conducted by or on behalf of DPR’s Air Program.

References


CDFA, 2018a. Memoranda Addressing MITC Field Spike Recoveries. California Department of Food and Agriculture. Sacramento CA.


APPROVED: Original Approved By DATE: 11/09/18
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