State of California

Memorandum

To	:	Edgar Vidrio, EPM I Department of Pesticide Regulation Enviromental Monitoring Branch 1001 I Street Sacramento, CA 95814	Date: Place: Phone:	November 2, 2018 Sacramento (916) 228-6829

From : **Department of Food and Agriculture** - 3292 Meadowview Road
Sacramento, CA 95832

Subject : **Field Spikes for Air Monitoring Studies**

At the request of the Department of Pesticide Regulation's (DPR) Air Program the Center for Analytical Chemistry (CAC) is providing information regarding the current fortified field spike preparation process including limitations and potential challenges with alternative methods (i.e., gas phase spiking).

Current Preparation Process and Potential Challenges

Field blind spike samples are part of CAC's client quality control and quality assurance program to assess lab performance. This is a general methodology used for most field studies. In air monitoring studies however, analyte stability during pumping air samples is an additional component of the measurement system, as any loss during pumping can be traced through the spike's recovery. This is more involved than field sampling of liquid and solid materials such as water and soil, and contributes to additional accountability for spike recovery results. This creates an additional quality assurance measure that is very difficult to quantify and track in the measurement system.

Blind spike submission is part of DPR's Environmental Monitoring Branch Quality Assurance/Quality Control (QA/QC) program which is described in Standard Operating Procedure (SOP) QAQC001.00. The Environmental Analysis Lab prepares the spike samples in accordance with DPR's specification for study of specific analytes and targeted concentration range. Under an agreement with DPR, CAC prepares blind spike for air samples using a spiking solution. Spike solutions are prepared in the same solvents used in extraction processes. Multi-residue analytes are prepared in acetone, Methyl Isothiocyanate in 0.4% carbon disulfide in ethyl acetate, and chloropicrin in hexane.

Use of liquid spiking solutions as a measure of QA/QC is consistent with validation and method detection limits for the air methods. In the lab, the resin trapping efficiency of each tube was also evaluated and determined using a liquid spiking solution by adding a known amount of the analyte to the tube. The tubes were then subjected to ambient air sampling for selected sampling time and flow rates. This is assumed to give an approximation of the efficiency in the recovery of the analytes both during the sampling and during the extraction of the analyte from the tube.

In case of fumigants and volatile compounds and gases, use of this QA/QC measure becomes challenging depending on chemical and physical properties of compounds. Challenges consist of low spike recoveries due to loss of chemical from volatilization and degradation and due to any effect of other field variables such as humidity and temperature during sampling with the pumps. Additionally, spiking methodology for gases and volatile chemicals becomes challenging as it is difficult to spike compounds in the same form and condition as analytes appear in the sampling environment. Generally spiking with solutions is the most feasible method of spiking in the lab. But depending on compounds it may not be representative of compound's characteristic in ambient air as chemicals in solution exhibit different properties than in ambient air depending on the solvent and their solubility.

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. Although the aim is to measure the quality of measurement results from the lab, it does not account for specific variables contributing to low 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 (measurements in the lab, sampling in the field, transportation, etc.) without the ability to isolate analyte loss at each step.

The lab applies this spiking method with intention to measure resin trapping efficiency and method performance in the laboratory. This approach may not account for other variables in the field that can impact spike recoveries. Resin trapping may be affected by variable humidity and temperature. Both of these field variables contribute to low recoveries of spikes. Without an ability to measure these variables this methodology is not a meaningful way of measuring analyte stability during study, transport, and lab's proficiency.

Only laboratory performance may be measured with this methodology. Spiking a tube with an aliquot of a liquid solution is an easy and accurate way for the lab to place an exact known amount of an analyte onto the sorption tube.

Alternative Preparation Process and Potential Challenges

Spiking using a gas phase process is a possible solution for those chemicals that exist in gas phase and will not include all the monitored pesticides for the multi-residue screen. However, it is costly and resource intensive requiring trained field staff and can not be administered by lab personnel. The following items are needed to spike samples using a gas phase process.

A custom blended gas standard would need to be purchased costing up to $1,000.00 per standard. The concentration of this standard would need to allow for approximately 1.0 µg of the analyte to flow onto the tube over the course of the normal sampling duration. The flow of the spiking gas would need to be low compared to the flow of the ambient air sampling. A flow of approximately 10 mL per minute would work well for this purpose.

A sampling manifold would need to be set up at each field sampling site. A spike sample would be prepared at a cost of between $2,000.00 to $3,000.00. The gas manifold would need to be electrically controlled either by plugging into an electrical source or using battery power. The gas manifold would allow the electronic flow control of the gas standard onto the tube during the entire sampling period, which would then give the best possible approximation of sampling efficiency during the sampling at the same sampling conditions of temperature and humidity as that of a non-spiked sample.

The electronic flow control can be used in the lab to put a known amount of an analyte into the sampling tube, although it will still be costly and resource intensive as described above. The limitation of this method is that the sampling conditions of varying temperature and humidity will not be reflected in the gas phase spike as in previous liquid spike methodology. A spike prepared in the laboratory using the gas phase process would give an approximation of the efficiency for the sampling if this gas phase spike was then sent to the field and sampled over the sampling period.

Sincerely,

Maryam Khosravifard
Environmental Program Manager I

Enclosure

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