APPENDIX A:
Technical System Audit of the California Department of Pesticide Regulation

Air Resources Board

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March 22, 2012

Mr. Randy Segawa
Environmental Program Manager
Department of Pesticide Regulation
California Environmental Protection Agency
1001 I Street
Sacramento, California 95812

Dear Mr. Segawa:

Attached is the final technical system audit (TSA) report for the Pesticide Air Monitoring Program. I would like to thank you for your assistance during the system audit process and for responding to the preliminary draft TSA report (response letter dated February 2, 2012).

ARB has reviewed your responses to the draft TSA report and would like to thank you for the thorough responses. ARB has updated the findings and recommendations in the final TSA report based on the additional information provided, with the following exceptions or qualifications:

Field Operations - Item 11

- Site photos and drawing from the March 15, 2011 audit indicate a tree within 40 feet of the probe inlet (located in a playground area). If the tree has been trimmed or removed since the audit, the tree is no longer a possible obstruction. However, if the tree is still present, the tree should be monitored to ensure it does not become a possible obstruction. (See Appendix C in final report)

Laboratory Operations - Items 5 and 6

- The response letter states that DPR and CDFA have a practice in place for handling multiple calibration curves and duplicate analyses. QAS recommends both agencies consider incorporating a decision-tree in the analytical SOP to describe the process and to ensure transparency to outside data users.

Laboratory Operations – Item 11

- The response letter states the cause of the low recoveries for Iprodione and MITC in blind spikes was identified and that procedures to correct the issues have been implemented. DPR should document the findings of the investigation and the corrective action taken. In addition, DRR should evaluate the possible impacts to the program data, and correct or invalidate the data as necessary.

Additionally, Field Operations Items 7 and 9 from the draft report have been removed from the final report based on the additional information provided in your response letter.

If you have any questions or need additional information regarding the report, please contact Patrick Rainey at (916) 327-4756 or by email at prainey@arb.ca.gov.

Sincerely,

/s/

Merrin Wright, Manager
Quality Assurance Section
Monitoring and Laboratory Division

Attachment

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TECHNICAL SYSTEM AUDIT OF THE CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION 2012

Conducted by:
California Air Resources Board
Monitoring and Laboratory Division
Quality Assurance Section

3/22/2012

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I. EXECUTIVE SUMMARY

Per the request of the California Department of Pesticide Regulations (CDPR), the California Air Resources Board (ARB) conducted a technical system audit (TSA) of the pesticide air monitoring network established by CDPR in 2011. The monitoring network is operated by CDPR in cooperation with analytical support provided by the California Department of Food and Agriculture's (CDFA) Center for Agricultural Chemistry (CAC) Laboratory. This report presents the findings of the TSA conducted in 2011.

A TSA is one of the ways that ARB and CDPR can ensure that the data collected by the pesticide monitoring network meets the data quality objectives of the program. The TSA also included flow check audits of all the pesticide samplers in the network, providing an additional assessment of the overall quality of the program.

Staff from ARBs Quality Assurance Section (QAS) of the Monitoring and Laboratory Division (MLD) conducted the TSA. ARB staff provided a questionnaire to be completed by CDPR and CDFA staff and conducted interviews of management and staff from both agencies. The questionnaire and interviews covered various aspects of the pesticide air monitoring program including network design, field operations, laboratory operations, data handling procedures, and quality assurance.

One of the most important elements in the implementation of an air monitoring program is documentation. Appropriate documentation includes, but is not limited to, network monitoring plans, standard operating procedures for all aspects of an organization's program, data quality assessments, record of daily operations, and documentation of quality control and maintenance checks. Oversight of personnel and activities involved in the collection, analysis, and the processing and submittal of data is much more straightforward when procedures are standardized and responsible personnel record their compliance with these procedures. The pesticide monitoring program is both well organized and maintained; and generally meets the requirements outlined in the Draft Network Monitoring Plan (December 2010). However, the review did identify several areas to enhance the overall quality of the pesticide monitoring program. Examples include:

- Program documents and procedures should be reviewed on a regular basis, and updated as necessary to ensure they are accurate, reflect current practices, are finalized documents, and meet the requirements of the program.

- Field and laboratory records should be reviewed to ensure they are accurate and complete.

- Field and laboratory equipment and supplies should be verified on a regular basis to ensure they meet the requirements of the program.

- Flow audits of samplers should be conducted on an annual basis, and a TSA performed every three years to ensure the quality systems and practices remain

in place. Additionally, an audit sample program should be developed to allow evaluation of method performance against an independent source.

- A corrective action procedure should be implemented to identify and document anomalies and non-conformance issues (typographical errors, incomplete documentation, expired standards, QC results outside of criteria, procedural changes, etc.) occurring in field or laboratory operations. Documentation should include a record of corrective actions performed as a result of the events.

- Training of project personnel should be documented and reviewed on a periodic basis to ensure personnel are sufficiently trained and qualified to fulfill the required responsibilities.

The findings presented in the TSA are followed with recommendations to address the stated concern. If CDPR or CDFA management has alternate approaches to address the concerns identified, ARB will consider them. Finally, it is important to note that the findings in this TSA are not intended to be used to validate or invalidate pesticide monitoring data.

ARB would like to thank all the staff and management of CDPR and CDFA for their support and cooperation during the TSA.

II. INTRODUCTION

The California Department of Pesticide Regulation (CDPR) established an air monitoring network in three agricultural communities to expand CDPR's knowledge of the potential health risks of long-term exposure to pesticides. Shafter, Salinas, and Ripon were selected from a list of 226 communities based on pesticide use on nearby farmland and demographics of the surrounding community. The network was designed to provide information that can be used to evaluate and improve protective measures against pesticide exposure. The Center for Analytical Chemistry (CAC) laboratory of the California Department of Food and Agriculture (CDFA) is under contract with CDPR to perform sample analysis and data reporting in support of the pesticide monitoring program.

CDPR requested the Quality Assurance Section (QAS) of the Air Resources Board (ARB) to conduct a technical system audit (TSA) of the pesticide monitoring network. The TSA is an on-site review and inspection of the field and laboratory operations to assess compliance with established guidelines governing the collection, analysis, validation, and reporting of the pesticide data. The TSA was conducted in three phases. The first phase consisted of a pre-audit questionnaire provided to the field and laboratory personnel in order to gather information about field and laboratory operations and data management procedures. The second phase included an on-site observation and assessment of the field operations followed by a laboratory visit to observe and evaluate the laboratory operations, data management and reporting, and quality assurance/quality control procedures. The third phase consisted of an in-depth evaluation of the information gathered from the questionnaire and on-site evaluation. A draft TSA report summarizing the TSA process, findings, and recommendations was provided to CDPR for review and comment. The final TSA report includes changes based on comments provided by CDPR in the February 2, 2012 TSA response letter (Attachment A), as well as notation of corrective actions already implemented by CDPR and CDFA.

III. TECHNICAL SYSTEM AUDIT SUMMMARY

The TSA of the CDPR/CDFA Pesticide Monitoring program conducted in 2011 found the pesticide sampling and analysis programs to be both well organized and maintained. The programs generally meet the requirements outlined in the Draft Air Monitoring Network Study Plan (December 2010). The staffing levels appear to be sufficient to perform all of the required tasks, and the interviewed staff members were knowledgeable about the requirements of pesticide monitoring. The standard operating procedures (SOPs) for the field and laboratory operations and data handling procedures were generally thorough, well written, and readily accessible to personnel. The quality assurance and quality control procedures for the field and laboratory activities were found to meet the pesticide monitoring network requirements for content and frequency. The field, laboratory, and administrative facilities were well maintained, sufficiently stocked, and appeared to have adequate space to perform all required activities. All staff encountered during the TSA process conducted themselves in a courteous and professional manner. ARB staff recommends that CDPR continue to operate their pesticide monitoring network program in accordance with their established methods and procedures. ARB staff has provided several recommendations that should be incorporated to further enhance the overall quality of the pesticide monitoring program. The general recommendations are as follows:

- Program documents and procedures (monitoring plan, field and laboratory SOPs, forms and charts, etc.) should be reviewed on a regular basis to ensure they are accurate and reflect current practices. Updates should be made as appropriate and current versions disseminated to program personnel.

- Field and laboratory documentation (chain of custody (COC) forms, laboratory preparation sheets, etc.) should be reviewed to ensure they are thorough and complete.

- Analytical standards used for quantitation of sample results should have current certification dates and be verified against a second source where possible.

- Procedures should be established for the identification and documentation of nonconformances (typographical errors, incomplete documentation, expired standards, etc.) and the corrective actions taken as a result of these events.

- Data management procedures (backup, archival, destruction) should be reviewed to ensure they are accurately documented and consistent with program requirements.

- Training records should be established to document training and qualifications of project personnel. Records should include completed training as well as future training needs.

IV. NETWORK MANAGEMENT

Introduction

The purpose of this section is to evaluate the documents and procedures used to manage and operate the pesticide monitoring network. Additionally, this section will describe the air monitoring network design, and the relationship and responsibilities of the agencies participating in the program; CDPR and CDFA. The ARB review of the pesticide monitoring network is based on the network design and the sampling and analysis requirements described in the Draft Air Monitoring Network Study Plan (December 2010), and the SOPs used by CDPR and CDFA for field and laboratory operations. The following documents and SOPs were reviewed prior to the field and laboratory audits:

- Draft Air Monitoring Network Study: Long-term Ambient Air Monitoring for Pesticides in Multiple California Communities (December 2010).
- Instructions for Calibration and Use of SKC Inc. Personal Sample Pumps (EQAI001.00, last revision date 07/12/2001)
- Preparation of Air Sampling Tubes, Resin Jars, and Cartridges (FSAI001.01, last revision date 07/30/2003)
- Sample Tracking Procedures (QAQC003.02, last revision date 04/18/2005)
- Creating and Filling Out a Chain of Custody Record (ADMN006.01, last revision date 03/04/2004)
- Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory (QAQC004.01, last revision date 09/25/1999)
- Chemistry Laboratory Quality Control (QAQC001.00, last revision date 07/31/1995)
- Conducting a Trapping Efficiency Study for Air Monitoring Using Standard in Solvent (FSAI003.00, last revision date 06/19/2003)
- Determination of Selected Pesticides Collected on XAD-4 Resin by High Performance Liquid Chromatography Ion Mass Spectrometry and Gas Chromatography Mass Spectrometry (EMON-SM-05-002, last revision date 10/27/2008)
- Determination of Acrolein, Iodomethane, Carbon Disulfide, Cis-1,3 Dichloropropene, Trans-1,3 Dichloropropene, MIBK, and Bromomethane in Air Samples Collected in Summa Canisters (EMON-SM-05-019, last revision date 11/29/2010)
- Determination of Chloropicrin Desorbed from XAD-4 Resin Tubes (EMON 16.0, last revision date 10/14/1999)
- Determination of MITC in Air by GC/NPD or GC/TSD (EMON-SM-41.9, last revision date 05/25/2004)

CDPR is the public agency responsible for protecting California and its residents from adverse health effects caused by pesticide exposure. As part of CDPR's mandate for

“continuous evaluation” of currently registered pesticides, the agency implemented a statewide air monitoring network for measuring pesticides in various agricultural communities. CDPR evaluated and prioritized 226 communities in California as candidates for the study. The communities were prioritized based on the pesticide use (both within 5 miles and regional use) and demographics data (communities with higher populations of children, persons over 65, and persons who work on farms and close proximity to agricultural areas with high pesticide use). CDPR selected the communities of Ripon, Salinas, and Shafter as the sampling locations for the study. These three communities provide a good geographical distribution, meet the desired demographics, and have relatively high use for most of the selected pesticides. In 2011, CDPR started an ambient air monitoring program for pesticides in these three communities, which is scheduled to continue for a period of three or more years.

CDPR monitors pesticides based primarily on potential health risk. Higher-risk pesticides have higher priority for monitoring. Pesticides were selected based on the following criteria:

1) Pounds of use by area/region (indicator of exposure)
2) Volatility (indicator of exposure)
3) DPR risk assessment priority (indicator of toxicity)
4) Feasibility of including in multi-residue monitoring method

CDPR, as the lead agency, is responsible for network setup, monitoring, sample handling, and data management and report generation procedures. CDFA is responsible for preparation of the sampling media, analysis of collected samples, and reporting of sample results to CDPR. CDFA is also responsible for maintenance of the analytical data generated from the analysis of samples during the monitoring program.

The pesticide monitoring network consists of a combination of field monitoring stations, a sample staging and administrative facility, and a laboratory facility. The three field monitoring stations are operated by CDPR personnel and are located in Ripon, Salinas, and Shafter, California. (See Table 1 for sample locations and monitored parameters). The sample staging facility is operated by CDPR personnel and located in West Sacramento, California, and the laboratory facility is operated by CDFA and located in Sacramento, California.

The program requires the cooperative interaction of CDPR and CDFA personnel throughout the process, from the preparation of sample media to the generation of the final project report. Sample media, prepared by CDFA, is transferred to CDPR field personnel, who are responsible for the sample collection operation and delivery of samples to the CDPR staging/receiving facility in West Sacramento. CDPR personnel in West Sacramento are responsible for review of field documentation, generation of the Analytical Request Sheets, and proper storage of the samples until they are delivered to the CDFA-CAC laboratory. CDFA-CAC laboratory personnel are responsible for sample analysis and data review and reporting, as well as maintenance and archive of analytical data generated in support of the program. CDPR personnel are responsible

for administrative review of the analytical reports and generation of the final project reports.

TABLE 1- PESTICIDE MONITORING LOCATIONS AND PARAMETERS

Sampling Location	Monitored Parameters			
	Multi-pesticide residue (GC/MS & LC/MS) (EMON-SM-05-002)	MITC by GC-NPD (EMON-SM-41.9)	Chloropicrin by GC-ECD (EMON 16.0)	VOCs by GC/MS (EMON-SM-05-019)
Ripon, California	**X**	**X**	**X**	**X**
Salinas, California	**X**	**X**	**X**	**X**
Shafter, California	**X**	**X**	**X**	**X**

Note- Appendix A includes analyte lists for each of the above methods.

Recommendations for Network Management-

Item 1: The pesticide monitoring program was recently established and may likely evolve and change over time as the program develops.

Recommendations: The program documents (Monitoring Plan, SOPs, forms, etc.) and procedures should be reviewed on a routine basis to ensure they are current and accurately reflect the practices and policies in place for the pesticide monitoring program. Additionally, it may be beneficial to periodically gather appropriate personnel from CDPR and CDFA to discuss the lessons-learned and determine if improvements can be made to the program**. *(Note –Air Network documents will be revised and updated (if deemed necessary) every 12 months as part of the network quality control check)***

Item 2: CDPR requested that ARB's QAS conduct sampler flow checks and a system audit at the initiation of the monitoring program to verify that quality systems and practices were in place.

Recommendation: ARB recommends that flow checks be conducted on an annual basis and system audits be conducted every three years to ensure that the quality systems and practices remain in place, and changes and improvements to the program are verified by an independent source. ***(Note – DPR supports annual flow audits and system audits every three years.)***

V. OPERATIONS

Introduction

The purpose of this section is to evaluate the field and laboratory operations of the pesticide air monitoring network according to the guidelines and requirements included in the CDPR Draft Air Monitoring Network Study Plan (December 2010) and SOPs for the field and laboratory operations. The field and sample staging/receiving operations are performed by CDPR personnel, and the laboratory operations are performed by CDFA personnel.

ARB staff conducted interviews with field and laboratory operations staff of CDPR and CDFA. The interviews were conducted based on questions developed from the Network Study Plan, audit questionnaire responses, and standard operating procedures provided prior to the on-site evaluation. All staff interviewed were very accommodating in making themselves available for interviews, procedural reviews, and on-site assessments. The following personnel were interviewed during the audits:

Roger Sava - CDPR Sampling Crew Lead
Sue Peoples - CDPR Laboratory Liaison
Steve Siegel - CDFA-CAC Laboratory Supervisor
Jean Hsu - CDFA-CAC Laboratory Analyst
Jane White - CDFA-CAC Laboratory Analyst

ARB staff members conducting the TSA were Harnek Nijjar and Patrick Rainey.

A. FIELD OPERATIONS

The pesticide monitoring network includes three field monitoring sites (Ripon, Salinas, and Shafter) and a sample staging/receiving area in West Sacramento. The field sampling design and procedures are described in the Draft Air Monitoring Network Study Plan (December 2010) and the CDPR field operations SOPs (see Network Management section for a list of SOPs).

The sampler siting criteria included in the Network Study Plan are based on 40 CFR Part 58, and specify that sample inlets should have a minimum of 3 feet horizontal and vertical distance from supporting structures, be 65 feet from trees, have a distance from obstacles of at least twice the obstacle height, and have unobstructed air flow for 270° around the air sampling equipment. Sampling dates and times are randomized throughout the week in order to cover a variety of dates and times. Sampler flow rates are calibrated prior to initial deployment in the field and are checked on a weekly basis at the beginning and end of each sampling period. The air sampling pump should display a percent difference of less than 20 percent between starting and ending flow rates for the sample to be considered valid. A canister sample is considered to be valid if the pressure remaining after sampling is below -5 inches Hg.

Sample field log sheets are completed in the field with information on sampler location, date, start/stop time, initial and final flow rates, sample media ID, analyst/sampler name, and comments about any unusual conditions that occurred in the field. Samples are recovered by CDPR personnel and shipped with a completed chain of custody (COC) record to the CDPR sample receiving facility. Samples are transported in a cooler with dry ice until they arrive at the sample receiving facility, where they are stored in a freezer at or below zero degrees Fahrenheit until transfer to CDFA. Samples are stored for no longer than two weeks prior to shipment to the CDFA laboratory for analysis.

Sample analytes included in the program, require the use of different collection media and flow rates. AirChek pumps used for the collection of the multi-pesticide residue samples on XAD-2 resin are set at a rate of 15 L/min. The SKC Inc® personal pumps used for collection of Chloropicrin on XAD-4 resin are set to 1.5L/min, and those used for Methyl isothiocyanate (MITC) on coconut charcoal are set at a flow of 50ml/min. Evacuated summa canisters used for the collection of volatile organic compound (VOC) samples are filled with ambient air using a flow controller. All samples are collected for a 24 hour period, and flow rates are measured at the beginning and end of the sampling period. Once collected, sample tubes or cartridges are capped and wrapped in Ziploc bags for packing and transport. Canister samples are transported at ambient conditions, while sample tubes and cartridges are transported on dry ice and remain frozen until receipt at the West Sacramento facility.

CDPR West Sacramento facility staff is responsible for verification and documentation of sample condition and temperature upon transfer of custody from field personnel. Facility staff is also responsible for generation of the Analytical Request Sheets and proper storage and tracking of samples until they are relinquished to CDFA-CAC laboratory personnel for analysis. Analytical Request Sheets define the analyses, and associated analytes, that are to be performed for each sample.

The Quality Assurance Section conducted flow audits of the pesticide samplers at the Ripon, Shafter, and Salinas pesticide monitoring sites on March 15, 29, and 30, 2011, respectively. The audits were scheduled so that auditors could observe both the pre- and post-sampling flow checks and sample handling procedures during the course of the program. The flow checks were conducted using a mass flow meter (MFM) connected in series with each pesticide sampler through the sampling cartridge to simulate actual operating conditions. The MFM readings were corrected to actual flow and compared to the sampler's indicated or calculated actual flow. The pesticide sampler flow checks were performed on the SKC low-flow (50cc/min), medium-flow (1.5L/min) and high flow (15L/min) samplers at each of the sites. The flow rates for the summa canister (VOC) samples were not checked because the pre- and post-sampling vacuum readings were recorded by field staff to determine the total volume sampled. All audited samplers passed the established audit criteria of $\pm$10 percent. The audit results are shown in Table 2.

ARB also reviewed the field sampling procedures with field personnel, and evaluated sampler siting to determine compliance with siting criteria outlined in the Draft Air Monitoring Network Study Plan (December 2010).

TABLE 2: PESTICIDE SAMPLER FLOW AUDIT RESULTS

Sampling Location: Ripon, CA

Sampler ID	Media ID	Sampler Actual Flow	Audit Actual Flow	% Difference	Result
00147	CC00039	50.27	47.72	5.3	Pass
2317	CC00040	52.33	50.39	3.8	Pass
5280	CC00037	1.45	1.51	-4.0	Pass
00132	CC00038	1.45	1.44	0.7	Pass
6644	CC00042	14.43	14.26	1.2	Pass

Sampling Location: Salinas, CA

Sampler ID	Media ID	Sampler Actual Flow	Audit Actual Flow	% Difference	Result
00270	A00058	44.23	45.61	-3.0	Pass
07893	A00057	48.07	49.03	-2.0	Pass
07930	A00055	1.39	1.40	-0.7	Pass
00140	A00056	1.42	1.42	0.0	Pass
07901	A00054	14.29	14.30	-0.1	Pass

Sampling Location: Shafter, CA

Sampler ID	Media ID	Sampler Actual Flow	Audit Actual Flow	% Difference	Result
00079	B00048	52.86	50.14	5.4	Pass
07892	B00047	49.07	46.97	4.5	Pass
07894	B00046	1.54	1.45	6.2	Pass
00273	B00045	1.56	1.48	5.4	Pass
08004	B00043	15.25	15.12	0.9	Pass
07896	B00044	15.53	15.43	0.6	Pass

On May 24, 2011, ARB staff conducted an on-site evaluation of the CDPR sample receiving facility in West Sacramento. The facility is a staging area for sample collection media prior to field deployment, and storage and maintenance of samples after collection, prior to delivery to the CDFA-CAC laboratory for analysis. CDPR is responsible for generation of the Analytical Request Sheets and completion of field custody information before relinquishing samples to CDFA. The on-site evaluation included an assessment of the facility as well as a review of the practices and procedures for sample tracking, storage, and COC records.

Recommendations for Field Operations-

***Item 1*:** CDPR did not have a finalized SOP for the sampling of VOCs in summa canisters.

Recommendation: CDPR should complete the SOP for VOC sampling as soon as possible. A draft SOP should be developed to document the procedure until the formal SOP is completed. ***(Note- DPR staff is developing a draft SOP for VOC sampling to be used by Air Network field operators)***

***Item 2*:** The Analytical Request Sheets generated by CDPR had an incorrect SOP reference number for the Multi-Pesticide Residue analysis procedure (GC/MS and LC/MS).

Recommendation: The reference should be corrected to read EMON-SM-05-002, and a review process established to prevent future issues. ***(Note- The method reference SOP number was corrected to EMON-SM-05-002.)***

***Item 3*:** The control chart for Cypermethrin had a typographical error for UWL and LWL; both were noted as 122%.

Recommendation: The typographical error should be corrected, and a review process established to prevent future issues. ***(Note- The Cypermethrin LWL was corrected to 58%)***

***Item 4*:** Summa canisters are stored in the refrigerator at the CDPR sample handling facility after receipt from field, prior to deliver to CDFA lab. Refrigerated storage conditions differ from those outlined in SOP (EMON-SM-05-019).

Recommendation: Storage conditions should be consistent with those outlined in the applicable SOP (EMON-SM-05-019). ***(Note- The summa canister storage location has been changed to be consistent with the applicable SOP.)***

***Item 5*:** Chain of custody sheets were incomplete. “Relinquished/Accepted” lines were not initialed and “media type” was not filled out.

Recommendation: Chain of custody sheets should be filled out completely by field personnel. Consistent use of the peer review process should minimize or eliminate future occurrences. ***(Note- DPR has instructed field personnel to completely fill in all COC forms)***

***Item 6*:** The temperature of the refrigerator used for storage of field samples at the CDPR sample staging/receiving facility dropped below the acceptable criteria (in SOP) on several occasions, but no notation was made in logbook. The refrigerator temperature is manually recorded on a periodic basis, but not daily. The data is available for download and review if needed, but this option is not currently used.

Recommendation: Refrigerator temperature should be maintained within the acceptable range as specified in the SOP, and appropriate notations made in the logbook for temperature excursions. Additionally, refrigerator temperature(s) should be recorded daily to ensure sample integrity is maintained. ***(Note- HOBO temperature data loggers have been installed in appropriate refrigerators and freezers for daily temperature readings.)***

Item 7: CDPR routinely collects collocated samples for the low-flow (50cc/min) and medium-flow (1.5L/min) methods, but typically only submits the sample media with the best flow rate for analysis. The other sample is discarded prior to submittal to CDFA for analysis.

Recommendation: CDPR should consider retaining the extra sample until analysis and review of the primary sample results are completed. These samples may be used as backup sample if the primary sample is lost or compromised***. (Note- DPR agrees with the recommendation and has changed their practice on retention of back-up samples.)***

Item 8: CDPR appears to have a well-developed system for training of new field personnel by an experienced trainer, but the process is not documented.

Recommendation: CDPR should document the employee training procedure, and maintain a record of completed training***. (Note- DPR will institute an employee training record system to keep track of employees current training and list any training needed.)***

Item 9: The Ripon monitoring site had a tree located within 38 feet from the nearest sample inlet. According to the Network Study Plan, there should not be any obstruction within 65 feet from the nearest sample inlet. The tree did not appear to cause an obstruction at the time of the audit because it had no foliage (see Appendix C for photos).

Recommendation: The tree should be monitored for growth, which could cause an obstruction in the future***. (Note- DPR was not aware of the presence of a tree causing a potential obstruction at the Ripon monitoring site. ARB has included***

additional information and pictures taken during the March 2011 flow audit of the site. (see Appendix C and attached cover letter))

B. LABORATORY OPERATIONS

On May 24, 2011, ARB staff conducted an on-site evaluation of the CDFA-CAC Laboratory in Sacramento, California, which performs sample analysis and reporting in support of the Pesticide Monitoring Program. CDFA is responsible for preparation of sample collection media prior to field deployment, and analysis and reporting of sample data following field collection. CDFA is also responsible for maintenance and archival of the analytical data generated during the sample analysis process. The on-site evaluation included an assessment of the facility as well as a review of the procedures and practices for chain-of-custody, sample analysis, data reporting, and data maintenance and archive.

The CDFA-CAC laboratory receives samples from CDPR approximately every two weeks. Laboratory personnel measure and record the temperature of the samples upon receipt using a digital surface temperature gauge. Sample condition is evaluated, and samples are logged in with unique laboratory sample numbers. The chain of custody document is maintained throughout the complete sample analysis process. Laboratory records include sample identification number, sample type, receipt date, collection data (flow rate, time, and date), analysis date, and name of the analyst(s) working on the samples.

Sample analysis is performed according to the laboratory SOPs (see Network Management section for list of SOPs) for the analyses requested on the Analytical Request Sheet provided with the samples from CDPR. The laboratory currently supports four analytical procedures for samples in this program; Multi-Pesticide Residue by Gas Chromatography- Mass Spectrometry (GC-MS) and Liquid Chromatography-Mass Spectrometry (LC-MS), Volatile Organic Compounds (VOCs) by GC-MS, Methyl isothiocyanate (MITC) by Gas Chromatography-Nitrogen Phosphorous Detector (GC-NPD), and Chloropicrin by Gas Chromatography- Electron Capture Detector (GC-ECD). Appendix A and B include the analyte list and method detection and quantitation limits for each of the methods. A brief description of each of the methods is as follows:

- **Multi-Pesticide Residue Analysis by GC-MS and LC-MS**
  Samples collected on XAD-4 resin are extracted and analyzed for pesticide residues using GC-MS and LC-MS methods as described in method EMON-SM-05-002 (CDFA, 2008). Analysis includes a variety of fungicides, insecticides, herbicides, and defoliants. The breakdown products of chlorpyrifos, diazinon, dimethoate, endosulfan and malathion are also included in the multi-residue analysis method. Appendix A, Table 1 includes a complete analyte list.

- **VOCs Analysis by GC-MS**
  Samples collected in summa canisters are analyzed for VOC compounds by GC-MS using a method similar to U.S. EPA's Method TO-15. The SOP describing the details of the procedure is EMON-SM-05-002 (CDFA, 2008). If possible, MITC and chloropicrin will also be analyzed by this method. If the laboratory is not able to include these analytes in the method, separate samples will be collected and analyzed by different methods. Appendix A, Table 2 includes a complete analyte list.

- **MITC by GC-NPD**
  Samples collected on SKC Inc® coconut charcoal sample tubes are analyzed for residues of MITC by GC-MS as described in analytical method EMON-SM41.9 (CDFA, 2004). MITC extraction from the sorbent medium involves using carbon disulfide in ethyl acetate with subsequent analysis using GC with a NPD. Appendix A, Table 3 includes a complete analyte list.

- **Chloropicrin by GC-ECD**
  SKC Inc® XAD-4 sample tubes are analyzed for residues of chloropicrin by GC-ECD as described in CDFA Method: EM16.0 (CDFA, 1999). Each tube will be desorbed in hexane and analyzed by gas chromatograph equipped with GC-ECD as described in the laboratory analysis section. Appendix A, Table 4 includes a complete analyte list.

Recommendations for Laboratory Operations-

Item 1: CDFA does not currently incorporate a second source for analytical standards used in the analyses performed in support of this program. Stock standard solutions are typically prepared by two different chemists from a single source only, and compared to one another.

Recommendation: CDFA should investigate and purchase a second source of analytical standards of acceptable quality, wherever possible. The second source should be used to verify the primary standards used for sample quantitation. ***(Note- CDFA has experienced difficulty in locating reliable second source materials for their analytical standards, but has implemented a practice of generating standard solutions in duplicate, typically by separate chemists, and verifying results and calculations.)***

Item 2: The gaseous standard cylinder used for VOC analysis expired November 2010. A new cylinder was ordered in April 2011, but had not yet been received at the time of the audit.

Recommendation: Gaseous standards used for analysis should have current certification dates. A new gaseous cylinder must be procured as soon as possible, and used for analysis. The response of the new and expired cylinder should be compared to determine if there is any impact on data generated using the expired cylinder. If a

significant difference is found between the analyses, appropriate corrective action should be performed***. (Note- CDFA has acquired a new VOC standard, and the responses compared to the original gas standard. Results were found to be within their established acceptance criteria.)***

Item 3: Preparation of blind spikes is not documented. A sticker containing some of the preparation information is placed on the media tube, but no other documentation is maintained in a permanent record.

Recommendation: Preparation of blind spikes should be documented in a logbook or other permanent format. This documentation should be maintained with the project files. ***(Note- DPR agrees with the ARB recommendation and states that preparation of blind spikes is now documented, and a record retained.)***

Item 4: Field/Blind spikes are not prepared for VOC analysis.

Recommendation: CDFA should develop and implement a procedure for preparation of blind spikes for the VOC analysis. The VOC analysis is a recently implemented procedure for CDFA, and should therefore be checked to ensure the sample collection and analysis procedures are working properly***. (Note- The program still lacks the capability to generate blind spikes for the VOC analysis, but has trained a second analyst to perform the VOC analysis and is investigating options for generating the VOC blind spikes.)***

Item 5: Multiple calibration curves are typically run with each analytical sequence (bracketing before and after) but no specific procedure/policy exists for determining how calibration curves are used for sample calculations. The decision appears to be made on case-by-case basis.

Recommendation: The laboratory should have a documented procedure/policy in place to determine how the calibration curves are used, and sample values calculated. ***(Note- DPR/CDFA provided a description of the practices in place for handling multiple calibration curves and duplicate analyses. However, QAS recommends both agencies consider incorporating a decision-tree in the analytical SOP to describe the process and to ensure transparency to outside data users.)***

Item 6: Samples are analyzed in duplicate, but no specific procedure/policy exists for handling the duplicate analyses. (Sometimes average results are reported, and other times one or the other is reported.)

Recommendation: The laboratory should have a documented procedure/policy for evaluating duplicate analyses. ***(Note- See response to #5 above.)***

Item 7: CDFA does not maintain training files for laboratory personnel performing analysis of pesticides. The chemists working on the program have extensive

experience, but are learning new methods based on personnel changes within the agency.

Recommendation: CDFA should maintain training files of the laboratory personnel. ***(Note- DPR has agreed that the pesticide methods will be incorporated into the annual training procedures and records maintained for their ISO accreditation.)***

Item 8: Laboratory instruments do not each have unique IDs, which can be referenced in logbooks and analytical data.

Recommendation: Laboratory instruments should be assigned unique IDs, which can be referenced in logbooks and analytical data. ***(Note- Specific instruments have been identified to perform the air analysis, and each has been given a unique identification.)***

Item 9: Laboratory instrument reports do not include reference to instrument ID or analytical method used for analysis. Laboratory personnel did not know if the instrument software was able to include that information.

Recommendation: Laboratory staff should talk with the vendor about how/where that information can be included. This information may be needed to recreate system and method parameters in the future. ***(Note- CDFA has investigated options for including the requested information into the report and has concluded that it cannot be done without developing a custom report, which does not work well with the instrument (Agilent) software. However, the instrument ID is included on the tune report, which is included in the data package.)***

Item 10: No instrument repair/maintenance logbooks were available for the GC/MS instruments used for the VOC analysis.

Recommendation: The laboratory should maintain individual repair/maintenance log books for each instrument, and they should remain with the instrument. ***(Note- DPR and CDFA agree with the item and have started maintenance logbooks for each VOC instrument.)***

Item 11: Recoveries for Iprodione and MITC in blind spikes were very low, and outside of established control limits.

Recommendation: Laboratory staff should investigate the cause of the low recoveries and implement corrective action as required. Field sample data should be evaluated for potential impact, and flagged as appropriate***. (Note- Response states that the identified issues were investigated, and describes the cause and corrective action implemented for each issue. However, ARB recommends that CDPR and CDFA should evaluate possible impacts to the program data, and correct or invalidate the data if necessary.)***

VI. DATA MANAGEMENT

Introduction
A primary goal of a quality system is to ensure that data generated is of sufficient quantity and quality to meet the needs of its intended use. Achievement of this goal involves planning, implementation, and assessment of the data collection process. Documentation and verification of the data and quality systems are key steps in the generation of quality data. As part of the TSA, ARB staff evaluated CDPR's and CDFA's data handling, verification, validation, storage, and reporting procedures in support of the pesticide air monitoring program.

The data stream for the pesticide monitoring program begins with the documentation of the program objectives, and the policies and procedures that will be used to meet those objectives, and continues throughout the process to the generation of a final project report. The documents describing these procedures and policies include the Network Monitoring Plan and the administrative and procedural SOPs for field and laboratory activities.

A. DATA MANAGEMENT- FIELD MONITORING OPERATIONS

The field monitoring stations at Ripon, Shafter, and Salinas are operated and maintained by CDPR field personnel, which are responsible for the sample collection, handling, and documentation of field operations. Sampling schedules are managed by the CDPR Sampling Coordinator, and field operations are overseen by a Sampling Crew Lead. Field sampling data (collection date/times, sampler flow rate, media ID, observations, etc.) are manually recorded on COC forms at the time of collection, and undergo a multi-level peer review both in the field and again at the sample staging/receiving facility in West Sacramento. Samples are transported under COC to the sample staging facility, where they are maintained in secured conditions until transfer to the CDFA-CAC laboratory. Prior to transfer of samples to CDFA, an Analysis Request Sheet is generated, which outlines the required analysis for each sample, and accompanies the samples and COC documentation to CDFA.

B. DATA MANAGEMENT- LABORATORY OPERATIONS

Samples received at the CDFA laboratory are logged into the laboratory information database and assigned a unique laboratory ID. The temperature and conditions of the sample at the time of the receipt are recorded. After receipt and login, samples are stored in accordance with the conditions outlined in the appropriate SOP, and a laboratory COC record initiated. Sample custody is recorded and maintained on the laboratory COC form throughout sample processing, and included in the final report.

Sample processing procedures are performed according to the appropriate CDFA procedural SOPs, and the dates, times, and analyst(s) initials are recorded. All data undergoes a technical peer review by a second analyst, and a complete review of the full analytical data package is performed by the laboratory supervisor before signature

and release of the summary data report to the CDPR Laboratory Liaison. The Laboratory Liaison performs a third-level administrative review of the summary data report, which includes a sanity check of sample dates, analyses performed versus the Analysis Request Sheet and COC, and evaluation of current data versus the historical data.

Electronic data are stored on the instrument data station at CDFA for a period of two years, after which time it may be purged if disk space is needed for other data. Hard copy data are stored for a period of two years in an offsite storage facility maintained by CDFA, after which time it would be disposed of according to the agency records retention policy.

RECOMMENDATIONS FOR DATA MANAGEMENT

Item 1: Electronic data (analytical) generated by CDFA during the analysis of samples in support of the program is only maintained on the instrument PC; no backup procedure is currently implemented for electronic data.

Recommendation: CDFA should develop and document a procedure and schedule for backup of electronic data for this program to avoid loss. The program is scheduled to last for three or more years, so data generated at the start of the program could potentially be deleted prior to completion of the program. CDFA should develop a general electronic back up policy/procedure to cover all analytical data. ***(Note- CDFA will begin to back up all electronic data generated for the air analysis. Different methods and formats may be used for different analytical instrumentation.)***

Item 2: Electronic and hard copy data is only maintained for approximately 2 years due to space limitations and CDFA branch policy.

Recommendation: The pesticide monitoring study is a long-term program scheduled to last three or more years, so alternate record retention timelines may be required. CDFA and CDPR should define a project specific record retention policy and timeline if it differs from the CDFA branch policy of maintaining the hard copy and electronic data for only 2 years. ***(Note- Response states that data is currently maintained in a hardcopy format for five years, but this can be extended for air data if needed.)***

VII. QUALITY ASSURANCE AND QUALITY CONTROL

Introduction

Quality assurance is an important aspect of the pesticide air monitoring program, and encompasses both field and laboratory activities. The quality assurance process includes the development of goals and objectives, documentation and validation of field and laboratory methods, training of personnel, and on-going evaluation of method and program performance.

The Draft Air Monitoring Network Study Plan (December 2010) describes the goals and objectives of the pesticide monitoring program, along with the field and laboratory methodologies and quality control components that will be used. Operational SOPs, developed by CDPR and CDFA, further describe the specific methods and procedures used by field and laboratory personnel, and define specific method performance components.

Prior to the analysis of field samples, field and laboratory personnel validated the sampling and analysis methods used for the monitoring program. The validation was performed by analyzing a series of spiked samples to document the precision and accuracy of the methods, performing trapping efficiency tests to verify analyte retention and check for chemical transformation of the adsorbed pesticides, and conducting storage stability tests to establish the stability of samples from the time of collection to analysis. Study results were used to establish upper and lower warning and control limits (± 2 and ± 3 standard deviations, respectively) for each analyte based on the average percent recovery of the validation replicate spikes. These limits are intended to remain static for the duration of the program, but may be updated if significant changes are observed based on the on-going accuracy and precision data derived from the field and laboratory QC samples.

On-going performance of the field and laboratory methodologies is determined through the collection and analysis of QC samples. Field QC samples include trip blanks, fortified field spikes, and collocated duplicate samples. Laboratory QC samples include laboratory blanks and laboratory control spikes. A description of each of the QC samples is as follows:

Trip blank is a “blank” sample tube or canister containing no pesticide residue. Upon collection of all field samples for that week, the end caps of a trip “blank” are momentarily removed or broken and the tube is then immediately re-capped. The canisters remain unopened. Air is not pulled through any of the trip blank samples. The “blank” samples are placed with the study samples and transported together until receipt at the West Sacramento facility. If pesticide residue is detected in any of the blank samples, action will take place to reassess field and laboratory procedures.

Fortified field spikes are sample tubes that have a known quantity of pesticides prepared and added by the laboratory. Following laboratory preparation, field spikes are transported at the beginning of the week’s sampling period where they are stored on

dry ice until needed. Fortified field spike tubes are then placed on the second set of air sampling pumps housed in the portable shelter and operated under the same conditions as the primary air sampler pumps. Comparison of the fortified sample and field sample pesticide recovery at the same monitoring location will provide information on any change in the ability to recover the pesticides under field conditions. Should fortified field spike pesticide recoveries fall outside the preset recovery control limits, a reassessment of the field and laboratory procedures would be conducted.

Duplicate samples are samples collected adjacent to the study samples under the same conditions as the primary air sampler. Pesticide recovery from the duplicate and primary samples is used to evaluate laboratory analytical precision; samples with greater than 50 percent difference in pesticide residue concentration will result in reassessment of the field and laboratory procedures.

Laboratory blanks are unexposed sample media or reagent taken through the laboratory sample preparation and analysis procedures to check for potential contamination in the laboratory processes.

Laboratory control spikes are sample media or reagent fortified with a known quantity of pesticides prepared by the laboratory, which are taken through the laboratory preparation and analysis procedures to monitor the on-going precision and accuracy of the analytical methodology.

At a minimum, one of the above field QC sample types (trip blank, fortified spike, duplicate sample) is collected at one site every other week, which results in a minimum of eight of each QC type at the end of each sampling year. Laboratory QC samples are included for each batch of ten or fewer field samples.

The program incorporates several criteria for assessing the performance of the field and laboratory operations. These include criteria for pre- and post-sampling flow rates, precision between duplicate samples, recovery of field spikes and laboratory control spikes, and cleanliness of field trip and laboratory blanks. Currently the program does not include data completeness criteria for the field and laboratory operations.

Field or laboratory corrective action may be taken if recoveries for blank, spiked, or duplicate QC samples fall outside the established limits. Method control charts are generated for each analyte on a periodic basis to assess on-going method performance and determine if further action is required.

The monitoring program was only initiated several weeks prior to the on-site evaluation, so only limited QC data was available for review. The laboratory control charts showed that the QC data was generally within the established control limits; with the exception of one data point each for Iprodione, MITC, Methidathion and Chlorthalonil that had recoveries below the limits.

RECOMMENDATIONS FOR QUALITY ASSURANCE

Item 1: The network Monitoring Plan and several of the field operations SOPs (see Field Operations section for specific SOPs) used in the program were not finalized at the time of the audit.

Recommendation: CDPR should finalize the Monitoring Plan and field SOPs as soon as possible. If policies or procedures change during the duration of the program, documents can be updated and assigned a new revision number to reflect the changes. ***(Note- DPR is in the process of preparing all SOPs needed for the air network.)***

Item 2: CDFA does not currently have a schedule or procedure established for the review and update of laboratory SOPs used for the pesticide monitoring program. The SOPs do not always reflect and document current practices and procedural changes.

Recommendation: CDFA should review and update as necessary all SOPs used for this program. Additionally, CDFA should develop a schedule to ensure documents reflect current practices, and utilize the Revision Log sheet for each SOP to document changes and implementation date for revisions. ***(Note- DPR and CDFA will incorporate all air SOPs and methods into their annual training program that is established for the ISO 17025 program.)***

Item 3: CDFA does not currently have an audit sample program in place for all program methods in order to validate sample handling and analysis procedures.

Recommendation: CDFA should investigate the availability of audit samples for the analytical methods used for the pesticide monitoring program, and incorporate where available. ***(Note- DPR states that ISO 17025 allows for the use of different options, based on availability, to monitor ongoing methods performance, and the use of client-specified blind spikes fulfills the criteria. However, ARB believes that DPR and CDFA should continue to develop a procedure for preparing blind spikes for the VOC analysis, and investigate options for acquiring custom-made blind spike samples from commercial vendors for other methods where available.)***

Item 4: The program currently has performance criteria established for certain aspects of the field and laboratory operations, but should consider establishing precision criteria for field and laboratory spikes and data completeness criteria as part of the monitoring network plan.

Recommendation: The program should establish precision criteria for the field and laboratory spikes, and completeness criteria for the overall program. These parameters can be evaluated when sufficient data is available***. (Note- CDFA performs only a single spike with each analytical batch, so precision cannot be determined. However, CDFA has historically generated control charts to monitor recoveries of the spiked samples versus the recovery limits calculated from the original validation data. Recently the laboratory has experienced a problem with the***

control chart software, and is working with the Information Technology group to identify replacement software for generating control charts.)

Item 5: A review of the available QC data indicated that recoveries were outside of the established control limits for several compounds (Iprodione, MITC, Methidathion, Chlorthalonil) in one or more of the field or laboratory spike aliquots.

Recommendation: CDFA should investigate the source of the low recoveries and perform corrective action as appropriate***. (Note- DPR provided additional clarification that the laboratory investigates all spike recoveries found to be outside of control limits. The source of the identified problems were investigated and corrected.)***

Item 6: CDPR and CDFA appear to have well developed procedures for training of personnel on new procedures or techniques, but the process did not seem to be documented. In addition, training files are not maintained for personnel participating in the monitoring program. Personnel working on the program have extensive experience with the agency(s), but are learning new methods based on personnel or programmatic changes within the agency.

Recommendation: CDPR and CDFA should maintain training files for all personnel involved with this project. ***(Note- DPR and CDFA will include training on all relevant SOPs in the annual training schedule.)***

Item 7: CDFA supports a variety of analytical programs, having different regulatory and programmatic QA/QC requirements. Some programs, such as ISO17025, have stringent management and technical requirements, while other have less stringent requirements. Maintenance of multiple QA/QC programs may cause confusion for laboratory personnel and difficulty for the Quality Assurance group to manage.

Recommendation: The pesticide monitoring program does not currently require, nor is it part of the ISO17025 program. ARB recommends that CDFA investigate the possibility of incorporating the pesticide monitoring program into the QA/QC structure developed by the laboratory to support ISO17025 programs. ARB believes it may address some of the issues of standards verification, training, and document review identified during the TSA. ***(Note- Response states that each environmental program has its own unique quality control requirements. SOPs include the specific QC requirements so all chemists and reviewers can ensure the requirements are met. The response states that no single QA/QC program can meet all requirements for the many programs supported by the laboratory.)***

APPENDIX A

(ANALYTICAL METHODS AND TARGET ANALYTES)

TABLE 1: Target Analytes in Multi-Pesticide Residue Analysis by GC/MS & LC/MS with XAD-4 Resin.

Pesticide	Product Name	Pesticide Group	Chemical Class
Acephate	Orthene	Insecticide	Organophosphate
Bensulide	Prefar	Herbicide	Organophosphate
Chlorothalonil	Bravo	Fungicide	Chloronitrile
Chlorpyrifos	Dursban	Insecticide	Organophosphate
Chlorpyrifos (Oxy Analog)	-		Organophosphate
Chlorthal-dimethyl	Dacthal	Herbicide	Phthalate
Cypermethrin	Demon	Insecticide	Pyrethroid
Diazinon	Various names	Insecticide	Organophosphate
Diazinon (Oxygen Analog)	-		Organophosphate
Dicofol	Kelthan	Insecticide	Organochlorine
Dimethoate	Cygon	Insecticide	Organophosphate
Dimethoate (Oxygen Analog)	-		Organophosphate
Diuron	Karmex	Herbicide	Urea
Endosulfan	Thiodan	Insecticide	Organochlorine
Endosulfan Sulfate	-		Organochlorine
EPTC	Eptam	Herbicide	Carbamate
Iprodione	Rovral	Fungicide	Dicarboximide
Malathion	Various names	Insecticide	Organophosphate
Malathion (Oxygen Analog)	-		Organophosphate
Methidathion	Supracide	Insecticide	Organophosphate
Metolachlor (S-metolachlor)	Dual	Herbicide	Chloracetanilide
Naled as dichlorvos (DDVP)	Dibrom, Vapona	Insecticide	Organophosphate
Norflurazon	Solicam	Herbicide	Pyridazinone
Oryzalin	Surflan	Herbicide	Dinitroaniline
Oxydemeton-methyl	Metasystox-R	Insecticide	Organophosphate
Oxyfluorfen	Goal	Herbicide	Diphenyl ether
Permethrin	Ambush	Insecticide	Pyrethroid
Phosmet	Imidan	Insecticide	Organophosphate
Propargite	Omite	Insecticide	Organosulfite
Simazine	Princep	Herbicide	Triazine
SSS-tributylphosphorotrithioate	DEF	Defoliant	Organophosphate
Trifluralin	Treflan	Herbicide	Dinitroaniline

TABLE 2: Target Analytes (VOCs) in Canister Residue Analysis by GC/MS.

Pesticide	Product Name	Pesticide Group	Chemical Class
1,3-dichloropropene	Telone, Inline	Fumigant	Halogenated organic
Acrolein	Magnacide	Algaecide	Aldehyde
Methyl Bromide		Fumigant	Halogenated organic
Sodium tetrathiocarbonate as carbon disulfide	Enzone	Fumigant	Inorganic
Methyl iodide	Midas	Fumigant	Halogenated organic
MITC*	Vapam, K-Pam, Dazomet	Fumigant	
Chloropicrin*		Fumigant	Halogenated organic

*analytes may be collected on sample tubes if they cannot be added to canister method.

TABLE 3: Target Analyte (MITC) in Coconut Charcoal by GC-NPD.

Pesticide	Product Name	Pesticide Group	Chemical Class
MITC*	Vapam, K-Pam, Dazomet	Fumigant	

*analyte may be included in canister method.

TABLE 4: Target Analyte (Chloropicrin) in XAD-4 Resin by GC-ECD.

Pesticide	Product Name	Pesticide Group	Chemical Class
Chloropicrin*		Fumigant	Halogenated organic

*analyte may be included in canister method.

APPENDIX B

(METHOD DETECTION AND QUANTITATION LIMITS)

TABLE 1: Detection and Quantitation Limits for Monitored Pesticides.

Pesticide or Breakdown product	Method Detection Limit (ng/m^3)	Quantitation Limit (ng/m^3)
Acephate	1.02	9.3
Acrolein	124	2,293
Bensulide	1.39	9.3
Chlorothalonil	13.7	23.1
Chloropicrin	TBD	TBD
Chlorpyrifos	5.05	23.1
Chlorpyrifos oxygen analog	2.92	9.3
Chlorthal-dimethyl	1.67	23.1
Cypermethrin	4.68	23.1
Diazinon	1.16	9.3
Diazinon oxygen analog	2.08	9.3
Dichlorvos (DDVP)	3.24	23.1
1,3-dichloropropene	TBD	
Dicofol	2.13	23.1
Dimethoate	2.31	9.3
Dimethoate oxygen analog	1.94	9.3
Diuron	5.14	9.3
Endosulfan	3.24	23.1
Endosulfan sulfate	4.63	23.1
EPTC	1.67	23.1
Iprodione	1.06	23.1
Malathion	2.18	23.1
Malathion oxygen analog	1.30	9.3
Metam-sodium (MITC)	5.56	
Methidathion	1.44	9.3
Methyl bromide	396	5,805
Methyl iodide	337	5,805
Metolachlor		9.3
Norflurazon	3.75	9.3
Oryzalin	1.39	23.1
Oxydemeton-methyl	2.31	9.3
Oxyfluorfen	6.39	23.1
Permethrin	7.22	23.1
Phosmet	7.96	9.3
Propargite	3.80	23.1
SSS-tributyltriphosphorotrithioate (DEF)	1.76	9.3
Simazine	1.20	9.3
Sodium tetrathiocarbonate as Carbon disulfide	324	3,114
Trifluralin	1.67	23.1

-Detection and quantitation limits are approximate for a 24-hour sample and will vary with the amount of air sampled and interferences present.
-TBD = to be determined.

APPENDIX C

(RIPON MONITORING SITE PHOTOS)

DANGER
HIGH VOLTAGE
KEEP OFF

ATTACHMENT A

(DPR DRAFT PESTICIDE TSA RESPONSE LETTER)

Department of Pesticide Regulation

Edmund G. Brown Jr.
Governor

M E M O R A N D U M

TO: Merrin Wright, Manager
Air Resource Board
1927 13th Street
Sacramento, California 95812

FROM: Randy Segawa, Environmental Program Manager *Original signed by*
Environmental Monitoring Branch
916-324-4137

DATE: February 2, 2012

SUBJECT: DEPARTMENT OF PESICIDE REGULATION'S RESPONSE TO COMMENTS PROVIDED ON THE AIR RESOURCES BOARD'S PRELIMINARY DRAFT TECHNICAL SYSTEM AUDIT OF THE PESTICIDE AIR MONITORING PROGRAM

Background

On November 17 2011, California Air Resources Board (ARB) submitted to California Department of Pesticide Regulation (DPR) a preliminary draft technical system audit (TSA) report of DPR Pesticide Air Monitoring Program as requested by the Environmental Monitoring Branch. This memorandum contains the DPR's responses to comments and suggestions made by ARB in the preliminary TSA report of the Air Monitoring Program.

DPR would like to thank ARB's Quality Assurance Section of the Monitoring and Laboratory Division for their keen observations and time placed for the system audit process. DPR's responses to the TSA audit comments are contained below.

If you have any questions or need additional information regarding the memorandum, please contact Edgar Vidrio at 916-323-2778 or <evidrio@cdpr.ca.gov>.

Attachment

cc: Pamela Wofford, DPR Senior Environmental Scientist
Edgar Vidrio, DPR Environmental Scientist
Sue Peoples, DPR Staff Environmental Scientist
Patrick Rainey, ARB
Michael Miguel, ARB
Harnek Nijjar, ARB
Stephen Siegel, CDFA

ARB's technical system audit report comments with the DPR responses

Network Management (page 10)

1. Item 1:
   The pesticide monitoring program was recently established and may likely evolve and change over time as the program develops.
   Recommendation*:* The program documents (Monitoring Plan, Standard Operating Procedures (SOP's), forms, etc.) and procedures should be reviewed on a routine basis to ensure they are current and accurately reflect the practices and policies in place for the pesticide monitoring program. Additionally, it may be beneficial to periodically gather appropriate personnel from DPR and California Department of Food and Agriculture (CDFA) to discuss the lessons-learned and determine if improvements can be made to the program.

DPR response:
All Air Network documentation will be revised and updated (if deemed necessary) every 12 months as part of a network quality control check.

2. Item 2:
   DPR requested that ARB's Quality Assurance Section conduct sampler flow checks and a system audit at the initiation of the monitoring program to verify that quality systems and practices were in place.
   Recommendation*:* ARB recommends that flow checks be conducted on an annual basis and system audits be conducted every three years to ensure that the quality systems and practices remain in place, and changes and improvements to the program are verified by an independent source.

DPR response:
DPR agrees to ARB's recommendation and will perform annual flow checks and system audits every three years.

Field Operations (pages 14-15)

1. Item 1:
   DPR did not have a finalized SOP for the sampling of Volatile Organic Compounds (VOCs) in summa canisters.
   Recommendation*:* DPR should complete the SOP for VOC sampling as soon as possible. A draft SOP should be developed to document the procedure until the formal SOP is completed.

DPR response:
DPR staff is developing a draft SOP for VOC Sampling to be used by Air Network field operators.

2. Item 2:
The Analytical Request Sheets generated by DPR had an incorrect SOP reference number for the Multi-Pesticide Residue analysis procedure (GC/MS and LC/MS).
Recommendation: The reference should be corrected to read EMON-SM-05-002, and a review process established to prevent future issues.

DPR response:
The reference method SOP number for the Multi-Pesticide Residue analysis was corrected to EMON-SM-05-002.

3. Item 3:
The control chart for Cypermethrin had a typographical error for UWL and LWL; both were noted as 122%.
Recommendation: The typographical error should be corrected, and a review process established to prevent future issues

DPR response:
The Cypermethrin LWL was corrected to 58.0%.

4. Item 4:
Summa canisters are stored in the refrigerator at the DPR sample handling facility after receipt from field, prior to deliver to CDFA lab. Refrigerated storage conditions differ from those outlined in SOP (EMON-SM-05-019).
Recommendation: Storage conditions should be consistent with those outlined in the applicable SOP (EMON-SM-05-019).

DPR response:
Summa canister storage location has been changed from refrigerator to a fire-resistant storage cabinet located next to the SR-10 refrigerator in the DPR sample handling facility prior to CDFA delivery.

5. Item 5;
Chain of custody sheets were incomplete. “Relinquished/Accepted” lines were not initialed and “media type” was not filled out.
Recommendation: Chain of custody sheets should be filled out completely by field personnel. Consistent use of the peer review process should minimize or eliminate future occurrences.

DPR response:
DPR has instructed its field personnel to completely fill in chain of custody sheets.

6. Item 6:
The temperature of the refrigerator used for storage of field samples at the DPR sample staging/receiving facility dropped below the acceptable criteria (in SOP) on several occasions, but no notation was made in logbook. The refrigerator temperature is manually recorded on a periodic basis, but not daily. The data is available for download and review if needed, but this option is not currently used.
Recommendation: Refrigerator temperature should be maintained within the acceptable range as specified in the SOP, and appropriate notations made in the logbook for temperature excursions. Additionally, refrigerator temperature(s) should be recorded daily to ensure sample integrity is maintained.

DPR response:
HOBO Temperature data loggers were installed in the SR-10 refrigerator and FR-5 and FR-6 freezers for daily temperature reading.

7. Item 7:
Trip blanks are not performed as part of the field quality control procedure, but are included in the monitoring plan.
Recommendation: Trip blanks should be instituted to assess possible contamination during transport of samples to and from the field. Additionally, field blanks should be performed periodically to assess possible contamination of the sampling equipment or sample handling techniques.

DPR response:
DPR has and continues to take trip blanks as part of the Air Monitoring Network's quality control. ARB's "Trip blanks" are the same as DPR's "sample blanks" which we have taken since the start of the monitoring network and continue to take periodically to assess possible contamination.

8. Item 8:
DPR routinely collects collocated samples for the low-flow (50cc/min) and medium-flow (1.5L/min) methods, but typically only submits the sample media with the best flow rate for analysis. The other sample is discarded prior to submittal to CDFA for analysis.
Recommendation*:* DPR should consider retaining the extra sample until analysis and review of the primary sample results are completed. These samples may be used as backup sample if the primary sample is lost or compromised.

DPR response:
DPR acknowledges the issue raised by ARB and has started to keep the unused collocated samples in storage until analysis and review of the primary sample results are completed.

9. Item 9:
The field spike sample procedure does not include background subtraction of the unspiked sample.
Recommendation: An additional nonspiked sample should be included to assess any contribution from field background. This would allow for a more accurate calculation of the field spike recoveries.

DPR response:
DPR disagrees with this observation as DPR does subtract any amount found in unspiked sample from the field spike.

10. Item 10:
DPR appears to have a well-developed system for training of new field personnel by an experienced trainer, but the process is not documented.
Recommendation: DPR should document the employee training procedure, and maintain a record of completed training.

DPR response:
DPR will institute an employee training record system to keep track of employees current training and list any training needed.

11. Item 11:
The Ripon monitoring site had a tree located within 38 feet from the nearest sample inlet. According to the Network Study Plan, there should not be any obstruction within 65 feet from the nearest sample inlet. The tree did not appear to cause an obstruction at the time of the audit because it had no foliage.
Recommendation*:* The tree should be monitored for growth, which could cause an obstruction in the future.

DPR response:
DPR is unaware of a tree being located 38 feet from the nearest sample inlet at the Ripon sampling site. The sampling location is located in an empty dirt field with no trees or other obstructions in sight.

Laboratory Operations (pages 17-19)

12. Item 1:
CDFA does not currently incorporate a second source for analytical standards used in the analyses performed in support of this program. Stock standard solutions are typically prepared by two different chemists from a single source only, and compared to one another.
Recommendation: CDFA should investigate and purchase a second source of analytical standards of acceptable quality, wherever possible. The second source should be used to verify the primary standards used for sample quantification.

DPR response:
We prepare each new standard in duplicate usually using a second chemist but, sometimes using the same chemist. The results of the duplicate analysis are checked to determine if they meet acceptance criteria. The results are reviewed by a second chemist to check for calculation errors. We have had a hard time finding a reliable source for our analytical standards. Almost all of our analytical neat standards come from Chem Service.

13. Item 2:
The gaseous standard cylinder used for VOC analysis expired November 2010.
A new cylinder was ordered in April 2011, but had not yet been received at the time of the audit.
Recommendation: Gaseous standards used for analysis should have current certification dates. A new gaseous cylinder must be procured as soon as possible, and used for analysis. The response of the new and expired cylinder should be compared to determine if there is any impact on data generated using the expired cylinder. If a significant difference is found between the analyses, appropriate corrective action should be performed.

DPR response:
The new VOC air mixture arrived at the lab on May 26, 2011. This was compared to the first gas standard which had an expiration date of November 30, 2010. The standards did not vary by more than 8% difference as calculated by difference/average X 100. The standards were again compared on January 19, 2012. The standards did not differ by more than 11% difference. This meets acceptance criteria for new standard preparation.

14. Item 3:
Preparation of blind spikes is not documented. A sticker containing some of the preparation information is placed on the media tube, but no other documentation is maintained in a permanent record.
Recommendation: Preparation of blind spikes should be documented in a logbook or other permanent format. This documentation should be maintained with the project files.

DPR response:
The blind spike preparation has been documented since the ARB audit was completed. The documentation was done in a logbook but the logbook was always getting misplaced. Now the documentation is done on a copy of the blind spike request. I have the standard identification, date prepared, expiration date and amount spiked listed. This is stored in a binder with all the blind spike requests located in the supervisor's office.

15. Item 4:
Field/Blind spikes are not prepared for VOC analysis.
Recommendation: CDFA should develop and implement a procedure for preparation of blind spikes for the VOC analysis. The VOC analysis is a recently implemented procedure for CDFA, and should therefore be checked to ensure the sample collection and analysis procedures are working properly.

DPR response:
We still do not have the capability to do VOC blind spikes. We have trained a second chemist to do the VOC analysis and this should allow the supervisor to develop a procedure for preparing the VOC blind spikes. A blending manifold still needs to be purchased for this procedure.

16. Item 5:
Multiple calibration curves are typically run with each analytical sequence (bracketing before and after) but no specific procedure/policy exists for determining how calibration curves are used for sample calculations. The decision appears to be made on case-by-case basis.
Recommendation: The laboratory should have a documented procedure/policy in place to determine how the calibration curves are used, and sample values calculated.

DPR response:
We analyze all samples here in duplicate. We first run a 5-point calibration curve, the Quality Control (QC) samples followed by the air samples. We then analyze another 5-point calibration curve, the QC samples followed by the air samples again. This is followed by the last 5-point calibration curve. We have acceptance criteria for the calibration curves (r must be greater than or equal to 0.995 for the correlation coefficient). The bracketing standards for a group of samples must meet the acceptance criteria of less than or equal to 20% difference. DPR evaluate the results on a run by run basis since we don't know the results until all the standards and

samples have been analyzed. If a calibration or bracketing standards do not meet acceptance criteria then we cannot report the results and we must use the other set of results if the acceptance criteria are met or the entire set of standards and samples need to be reanalyzed. The chemist evaluated the results and will choose how to report the results. DPR may use average results or just report the first or second injection results. The chemist indicates what results are reported in the data package.

17. Item 6:

Samples are analyzed in duplicate, but no specific procedure/policy exists for handling the duplicate analyses. (Sometimes average results are reported, and other times one or the other is reported.)

Recommendation: The laboratory should have a documented procedure/policy for evaluating duplicate analyses.

DPR response:

We always run samples in duplicate but we need to evaluate the sample results after each analysis has been completed to determine which results will be reported. Since, we have no criteria for the % relative standard deviation for duplicate sample injections; therefore, if both duplicate samples results are found to be within the acceptable criteria, then an average of both samples is reported. Likewise if only one sample is acceptable, then only that sample will be reported and the duplicate invalid sample result will be discarded. The acceptance criteria are the R^2 for the standard curves. For the curves to be acceptable, they must have an $R^2 \geq 0.990$. Each analytical set has up to 3 curves run with it, the beginning curve, middle curve, and an ending curve. The acceptance criterion for the samples is each curve must have an $R^2 \geq 0.990$. Therefore, if for instance the middle curve is less than 0.990, then all of the samples analyzed after this curve would be considered invalid.

Sometimes the sample results are better on either the first or second injection even though the acceptable criteria have been met for both analyses. If this is the case, the chemist will usually report what they determine to be the best results. It is hard to have written rules that state exactly how results should be reported since each sample set has its own unique problems. All reported results must meet all acceptance criteria before being reported.

18. Item 7:

CDFA does not maintain training files for laboratory personnel performing analysis of pesticides. The chemists working on the program have extensive experience, but are learning new methods based on personnel changes within the agency.

Recommendation: CDFA should maintain training files of the laboratory personnel.

DPR response:
We maintain training records for our International Organization for standardization (ISO) accreditation. These records show that the chemist has been trained and that the supervisor has authorized the chemist to perform a specific analysis. The training records also show that the chemists have reviewed our Quality Manual and any section procedures related to the sample analysis. This is done on a yearly basis. We will add in the method SOP's used for all the air analysis in the yearly training for the chemists.

19. Item 8:
Laboratory instruments do not each have unique identifications (IDs), which can be referenced in logbooks and analytical data.
Recommendation: Laboratory instruments should be assigned unique IDs, which can be referenced in logbooks and analytical data.

DPR response:
See DPR response for Item 9 listed below.

20. Item 9:
Laboratory instrument reports do not include reference to instrument ID or analytical method used for analysis. Laboratory personnel did not know if the instrument software was able to include that information.
Recommendation: Laboratory staff should talk with the vendor about how/where that information can be included. This information may be needed to recreate system and method parameters in the future.

DPR response:
We have identified specific instruments to do the air analysis. We have given each instrument doing air analysis a unique identification. For chloropicrin we use GC-D, for the MITC analysis we are using Varian 3800, For the VOC's we are using VOC instrument #1 or #2, for the GC/MS multi-residue we are using GCMS 3715 (the last 4 digits in the serial number) and for the Waters LC/MS we are using Waters Acquity UPLC with XEVO TQ #1. This identification will appear on the sample reports for all the analysis except for the VOC's and the GC/MS multi-residue analysis. We have checked into getting this information put into the sample report but we cannot do it unless we develop a custom report. Custom reports do not work well on the Agilent software. The instrument identification however does appear on the GC/MS tune reports which are included in the data package and well will write this into the sequence file for each instrument. The sequence files are included in the data package as well.

21. Item 10:
No instrument repair/maintenance logbooks were available for the GC/MS instruments used for the VOC analysis.
Recommendation: The laboratory should maintain individual repair/maintenance log books for each instrument, and they should remain with the instrument.

DPR response:
The maintenance logbook has been made for each VOC instrument.

22. Item 11:
Recoveries for Iprodione and MITC in blind spikes were very low, and outside of established control limits.
Recommendation: Laboratory staff should investigate the cause of the low recoveries and implement corrective action as required. Field sample data should be evaluated for potential impact, and flagged as appropriate.

DPR response:
The low recoveries for iprodione were due to using a spiking standard prepared in methanol. Iprodione breaks down in methanol causing the low recoveries. We prepared a spiking standard in ethyl acetate. Iprodione does not break down in this solvent. The recoveries of Iprodione have been good using this mix. There were problems with low recovery of MITC. The problem was a result of using a spiking standard at too low of a concentration requiring a large volume of the mix to be spiked onto the XAD absorbent. The large volume of solvent used lowered the recovery of MITC. We were adding up to 100µL of spiking solvent. We are now using a more concentrated spiking solution. Our spiking volumes are now 1-2 µL resulting in good recovery of MITC. There was also a problem with the recovery of chloropicrin which was due to spiking the solution onto the glass wool in the tube and not into the absorbent. This has been corrected by using a syringe with a longer needle.

Data Management (page 21)

23. Item 1:
Electronic data (analytical) generated by CDFA during the analysis of samples in support of the program is only maintained on the instrument PC; no backup procedure is currently implemented for electronic data.
Recommendation: CDFA should develop and document a procedure and schedule for backup of electronic data for this program to avoid loss. The program is scheduled to last for three or more years, so data generated at the start of the program could potentially be deleted prior to completion of the program. CDFA should develop a general electronic back up policy/procedure to cover all analytical data.

DPR response:
Currently the laboratory does not do electronic sample data backup. DPR will begin to do this for all air data. The GC/MSD's that the VOC's and the GC multi-residue analysis are analyzed on have built in DVD writers. The chemstation software allows back up of individual files for retention on these instruments. We have a piggy-back CD writer for our GC-ECD instrument and we will back up this data as well. For both the Varian and the Waters LC/LC the data is stored on the disk drive in a database format. We cannot back up individual files. DPR will be working with the Iinformation Technology Branch (ITB) to devise a procedure for backing up the sample data in the database format.

24. Item 2:
Electronic and hard copy data is only maintained for approximately two years due to space limitations and CDFA branch policy.
Recommendation: The pesticide monitoring study is a long-term program scheduled to last three or more years, so alternate record retention timelines may be required. CDFA and DPR should define a project specific record retention policy and timeline if it differs from the CDFA branch policy of maintaining the hard copy and electronic data for only two years.

DPR response:
Currently the laboratory keeps hard copy data stored offsite for five years. This can be extended for the air samples if needed.

Quality Assurance (pages 24-25)

25. Item 1:
The network Monitoring Plan and several of the field operations SOPs (see Field Operations section for specific SOPs) used in the program were not finalized at the time of the audit.
Recommendation: DPR should finalize the Monitoring Plan and field SOPs as soon as possible. If policies or procedures change during the duration of the program, documents can be updated and assigned a new revision number to reflect the changes.

DPR response:
DPR is currently preparing all of the SOPs needed from the air network.

26. Item 2:
CDFA does not currently have a schedule or procedure established for the review and update of laboratory SOPs used for the pesticide monitoring program. The SOPs do not always reflect and document current practices and procedural changes.
Recommendation*:* CDFA should review and update as necessary all SOPs used for this program. Additionally, CDFA should develop a schedule to ensure documents reflect current

practices, and utilize the Revision Log sheet for each SOP to document changes and implementation date for revisions.

DPR response:
This is addressed in Comment #20 above. We are going to add in all air SOP's and methods in our yearly training program that is established for the ISO 17025 program.

27. Item 3:
CDFA does not currently have an audit sample program in place for all program methods in order to validate sample handling and analysis procedures.
Recommendation: CDFA should investigate the availability of audit samples for the analytical methods used for the pesticide monitoring program, and incorporate where available.

DPR response:
During an ISO 17025 audit, the lab was told to get check samples from an approved vendor to check ongoing method performance. Currently, there are no commercially available check samples. There is however, companies that provide custom performance evaluation samples. The problem with these samples is that they can only monitor recovery data. Therefore, the CDFA lab is currently meeting the ISO 17025 requirements by utilizing client specified blind spikes to serve as validation as stated in the rule. Specifically, ISO 17025 5.9.1 (1) requires that for those test methods which are not covered by external Proficiency Testing schemes or if existing schemes are not suitable or feasible, the laboratory shall do its best to demonstrate competency for its scope. Alternate actions, listed in order of preference, are to participate in a round robin, inter laboratory comparison, comparison with another method or the use of Certified Reference Material, and/or internal quality control (client specified blind spikes- in our case), which was what Organophosphate method is presenting as a competency testing tool. This has been acceptable to A2LA (The American Association for Laboratory Accreditation) assessors.

28. Item 4:
The program currently has performance criteria established for certain aspects of the field and laboratory operations, but should consider establishing precision criteria for field and laboratory spikes and data completeness criteria as part of the monitoring network plan.
Recommendation: The program should establish precision criteria for the field and laboratory spikes, and completeness criteria for the overall program. These parameters can be evaluated when sufficient data is available.

DPR response:
The laboratory only does a single spike with each analytical batch of samples extracted. No precision data can be gathered from a single spike. The laboratory used to use control charts to track all spike recoveries. These control charts were reviewed by the person who does the final

review of the sample data. We reviewed them for recovery and trends. The recovery limits are specified in the spec sheet given to us by DPR which were calculated from validation data. The trends we look for are more than seven consecutive points either above or below the method average, points that are either increasing or decreasing over seven consecutive points. These trends may indicate that the method is going out of control. When these trends are identified by the reviewer the laboratory will look into the cause of the trends and check to see if there really is an out of control situation. Due to a problem with the software six months ago, currently we are not using control charts. DPR's ITB identified a problem with the control chart software that the lab was using and the ITB deleted this software. We are currently working with the ITB to order in replacement software so we can continue to monitor recoveries and trends in the sample results.

29. Item 5:
A review of the available QC data indicated that recoveries were outside of the established control limits for several compounds (iprodione, MITC, methidathion, and chlorthalonil) in one or more of the field or laboratory spike aliquots.
Recommendation*:* CDFA should investigate the source of the low recoveries and perform corrective action as appropriate.

DPR response:
Whenever a laboratory spike has recoveries outside the control limits the laboratory will investigate the cause. See Comment #24 above. The problem with chlorothalonil has been fixed by using a new 5975 GC/MSD instrument.

30. Item 6:
DPR and CDFA appear to have well developed procedures for training of personnel on new procedures or techniques, but the process did not seem to be documented. In addition, training files are not maintained for personnel participating in the monitoring program. Personnel working on the program have extensive experience with the agency(s), but are learning new methods based on personnel or programmatic changes within the agency.
Recommendation: DPR and CDFA should maintain training files for all personnel involved with this project.

DPR response:
See Comment #20 above. Training on all relevant SOP's will be included in our yearly training schedule.

31. Item 7:
CDFA supports a variety of analytical programs, having different regulatory and programmatic QA/QC requirements. Some programs, such as ISO17025, have stringent management and technical requirements, while other have less stringent requirements. Maintenance of multiple

QA/QC programs may cause confusion for laboratory personnel and difficulty for the Quality Assurance group to manage.

Recommendation*:* The pesticide monitoring program does not currently require, nor is it part of the ISO17025 program. ARB recommends that CDFA investigate the possibility of incorporating the pesticide monitoring program into the QA/QC structure developed by the laboratory to support ISO17025 programs. ARB believes it may address some of the issues of standards verification, training, and document review identified during the technical system audit

DPR response:

Each program that the environmental analysis laboratory supports has their own unique quality control requirements. Because of this all SOP's for methods done at the laboratory have the QC requirement written into them so all the chemists and the final reviewer will know the requirements and check to make sure the requirements have been met. No single QA/QC program can meet all requirements for the many programs that the laboratory supports.

APPENDIX B:
Memorandum on False Positives

State of California

Memorandum

To : Randy Segawa, Environmental Program Manager I
Department of Pesticide Regulation,
Environmental Monitoring Branch
1001 I Street
Sacramento, CA 95812-4015

Date: March 8, 2012
Place: Sacramento
Phone: (916) 262-1434

From : **Department of Food and Agriculture** - Center for Analytical Chemistry
3292 Meadowview Road
Sacramento, CA 95814

Subject : **S,S,S-tributyl phoshorotrithioate (DEF) Trace Detections**

"Trace" level detection is defined as the detection of an analyte concentration which falls between the reporting limit and the method detection limit. A trace detection is likely the analyte of interest based on the analysts' best judgment. The concentration quantified at this level should be suspect and is not accurate since the quantitation is far below the lowest calibration standard used. This definition was agreed upon between the Center for Analytical Chemistry and the Environmental Monitoring Branch in a memorandum dated July 17, 2002 titled Trace Detections of Pesticides in Surface Water Samples.

The following samples reported with "trace" levels of DEF are likely false positives:

Date received	Sample ID	DEF amount reported (µg/sample)
05/20/2011	A00099	0.006
06/06/2011	A00111	0.060
06/20/2011	A00126	0.019
07/01/2011	A00140	0.062
07/15/2011	A00157	0.064

It has been determined that these trace level detections were due to carryover from a spiked quality control sample that was analyzed just prior to the samples listed above. Sample sets prior to 05/20/2011 show no carryover.

The trace carryover was found in a sample analysis sequence when a sample was analyzed immediately following a spiked quality control sample or the highest concentration reference standard. These amounts detected are below the established reporting levels and reported as trace. These detections were initially not believed to be carryover because analyses by liquid chromatography do not generally produce carryover between samples. Normal operation of the

equipment provides a constant flow of solvent through the system which prevents analytes from staying in the system. However, with information that no DEF detections should be found in the areas sampled, lab personnel scrutinized the data sets again and noticed the carryover.

The samples were analyzed with a Waters Acquity UPLC / Xevo triple quadrupole mass spectrometer. The Center for Analytical Chemistry has been running the systems with wash cycles and wash solvents established by the manufacturer of the instrument. The instrument manufacturer has been contacted for assistance in determining why the carryover is occurring. The instrument uses small pumps, valves, tubing, and analytical columns to move solvent and samples through the system during analysis. Each part of the instrument that has contact with the samples and has a potential of causing analytes to be retained and carried over will be evaluated and tested. The manufacturer's engineers will be checking and optimizing the system this month.

Until the carryover issue is completely resolved, the lab is currently analyzing two solvent blanks after the five point calibration standard curve and the quality control spike samples. A second solvent blank consistently shows no carryover.

A sample set received 02/17/2012 has what the laboratory believes to be a trace DEF detection. The analyte was identified in the sample based on its consistency with the DEF standard, including the same retention time, isolation of the ionized parent compound with a mass/charge ratio of 315, and detection of two product ions with mass/charge ratios of 169 and 57. Sample C00353 showed 0.009 µgs/sample and was re-analyzed for confirmation and to ensure no possibility of carryover. The analyte was confirmed. This detection is not a result of any laboratory carryover since the previous sample definitively shows no DEF detection.

The Center for Analytical Chemistry could increase the reporting level for DEF, but this detection would still be reported as "trace".

Other analytes that have shown some carryover problems are:

Bensulide	Chlorpyrifos oxygen analog	Diazinon
Methidathion	Metolachor	

Trace level amounts of these five compounds were found in samples A000999, A00111, A00126, A00141 and A00157. These results are most likely to have resulted from carryover from the quality control spike samples analyzed just prior to these samples.

Samples have been re-evaluated and only the samples listed contain analyte carryover at trace levels. We have not found any other samples with carryover.

Possible modes of contamination within the laboratory have been discussed and are highly improbable. The levels found are from carryover due to analysis of standards and spikes just prior to the samples in question.

Sincerely,

Elaine Wong

Elaine Wong,
Environmental Program Manager I

Enclosure

Department of Pesticide Regulation

Paul E. Helliker
Director

Gray Davis
Governor
Winston H. Hickox
Secretary, California Environmental Protection Agency

MEMORANDUM

TO: Catherine Cooper
Agricultural Chemist III
Center for Analytical Chemistry
California Department of Food and Agriculture

FROM: Kean S. Goh, Ph.D.
Agricultural Program Supervisor IV
Environmental Monitoring Branch
(916) 324-4100

DATE: July 17, 2002

SUBJECT: TRACE DETECTIONS OF PESTICIDES IN SURFACE WATER SAMPLES

A primary goal of the Department of Pesticide Regulation's (DPR's) surface water program is to identify and control pesticides that cause toxicity to aquatic organisms. For some pesticides, toxic effects to sensitive aquatic species occur at concentrations less than current reporting limits. DPR's surface water program would benefit from the identification of samples that likely contain pesticides at concentrations less than the reporting limit. Therefore, the Environmental Monitoring Branch requests "trace" detections be reported on chain of custody sheets for all surface water matrix samples. We are defining trace detection as an analyte concentration that falls between the reporting limit and method detection limit. In addition, the chemist determines that the trace detection is likely due to the analyte of interest, in his/her best professional judgment. A trace detection does not require the chemist to be certain that the analyte is present in the sample, only that the analyte is likely to be present. A trace detection should not be reported if in the chemist's opinion it is likely due to an interference or other artifact or it is masked by the background. A trace detection does not require confirmation or unequivocal identification of the analyte. The word "trace" should be written on the chain of custody to document trace detections. Trace detections should not be quantified since they are likely less than the quantitation limit. The chemist may include additional qualifiers or descriptions of the trace detection on the chain of custody or separate document. This request only applies to surface water samples.

Thank you for your consideration of this request. Please contact me if you have any questions.

Approved by: John S. Sanders
John S. Sanders, Ph.D., Chief
Environmental Monitoring Branch

Date: 7/17/02

Department of Pesticide Regulation

Brian R. Leahy
Director

Edmund G. Brown Jr.
Governor

M E M O R A N D U M

TO: Elaine Wong, Branch Chief
California Department of Food and Agriculture
Center for Analytical Chemistry
Environmental Monitoring Section
3292 Meadowview Road
Sacramento, California 95832

Original signed by David Duncan
for

FROM: Randy Segawa
Environmental Program Manager
Environmental Monitoring Branch
916-324-4137

DATE: April 4, 2012

SUBJECT: ADDITIONAL ISSUES FOR S,S,S-TRIBUTYLPHOSPHOROTRITHIOATE TRACE DETECTIONS

Thank you for the information on the trace detections of S,S,S-tributylphosphorotrithioate for the air monitoring network (Study 257) provided in the memorandum dated March 8, 2012, and the conclusion that most of the detections were false positives due to instrument contamination caused by "carryover." There are some additional issues regarding these detections and carryover that I would like you to evaluate.

Issue 1: Evaluate some unusual duplicate and field blank results. The following samples contain detections in field blanks, or detections in one duplicate sample, but not the companion duplicate. Please determine if these detections are false positives. If some of these detections are false positives, it would confirm that detectable carryover occurred with other analytes. What can be done to check for false positives in the remaining samples?

- For field blank sample collected on 8/24/11
  #C00201: trace detection for malathion oxygen analog

- For field blank sample collected on 12/28/11
  #A00318: trace detection for malathion oxygen analog

- For duplicate samples collected on 2/15/12
  #C00353: trace detections for oxyfluorfen, S,S,S-tributylphosphorotrithioate, diuron, oryzalin, and simazine
  #C00354: No trace detections

- For duplicate samples collected on 2/9/12
  #B00335: trace detections for chlorpyrifos, chlorpyrifos oxygen analog, diuron, oryzalin, and simazine
  #B00334: No trace detections

- For duplicate samples collected on 1/12/12
  #B00308: 0.56 ug detection for chlorpyrifos; trace detections for chlorpyrifos oxygen analog, diuron, and simazine
  #B00314: No trace detections

- For duplicate samples collected on 9/6/11
  #B00192: trace detections for chlorpyrifos, and chlorpyrifos oxygen analog
  #B00193: No trace detections

Issue 2: Evaluate the possibility that some concentrations are underestimated. If carryover occurs, does this cause underestimation of the concentration in the standard or spike that had the carryover?

Issue 3: Evaluate the possibility of carryover from one field sample to another. Could we be getting false positives due to carryover from one field sample to another? What steps should be taken to prevent this from occurring?

Issue 4: Consider changes to data review. It seems like one of the reviewers should have noticed the detections in the solvent blanks earlier.

Issue 5: Evaluate the May-July 2011 sample collection period. The carryover apparently did not occur prior to May 2011 and the greatest carryover occurred with the false positives for S,S,S-tributylphosphorotrithioate during May-July 2011. Why is this?

Issue 6: Confirm that the instrument with carryover has not been used for other studies since it was received.

Issue 7: Should additional steps be taken to prevent false positives? Describe any additional steps taken to prevent false positives since the March 8th memorandum. Has Waters provided any useful information? Should we revise the detection limits for some analytes? Should we drop

some analytes from the method? Can we shift any of the analytes with carryover to the gas chromatography – mass spectrometer method? Do you have any recommendations for steps DPR should take to prevent false positives in the future, such as arranging for additional audits, or analysis of duplicate or split samples by a another laboratory?

Thank you for your continued assistance on these issues. Please feel free contact me if you have any questions or need further discussion.

State of California

Memorandum

To : Randy Segawa, Environmental Program Manager I
Department of Pesticide Regulation,
Environmental Monitoring Branch
1001 I Street
Sacramento, CA 95812-4015

Date: May 1, 2012

Place: Sacramento

Phone: (916) 262-1434

From : **Department of Food and Agriculture** - Center for Analytical Chemistry
3292 Meadowview Road
Sacramento, CA 95814

Subject : **Response to Additional Issues For S,S,S-tributyl phoshorotrithioate (DEF) Trace Detections**

This is a response to the memorandum dated April 4, 2012 which outlines additional issues and questions regarding trace detections and "carryover" of several pesticides from the air monitoring network Study 257.

The individual points associated with Issue 1 are addressed on an attachment to this response.

Issue 1:

The request to evaluate some unusual duplicate and field blank results has been completed. The review included all data packages associated with the air monitoring network Study 257 and it has been determined that the trace detections, other than those identified as carryover, are not false positives. The possibility of carryover is highly improbable on these samples. Based on the analytical comparison to certified reference standards, retention times, and two mass spectrometric transitions for these analytes, the trace amounts were correctly reported in the samples.

It would not be accurate to assume that carryover would occur with other analytes if some false positives were detected. The method is able to screen for more than 17 analytes, but each analyte has its own chemical properties and characteristics which provides for unique analytical profiles. Most liquid chromatography mass spectrometry uses methanol for analysis and this solvent shows no carryover problems. The analytes which showed carryover were prepared with ethyl acetate. Ethyl acetate is more chemically compatible than methanol for some analytes and offers better extraction and sensitivity for analysis. However, with the carryover issue, we are now evaluating the possibility of changing solvents.

The data review process has been updated to include stricter evaluations specifically for possible carryover and additional precautionary control samples are now being analyzed.

Issue 2:

The theoretical possibility concentrations are being underestimated does exist. All instrument manufacturers have a published level of potential carryover. The instrumentation in question has a published amount of 0.05 percent and is calculated based on total area counts, not concentrations.
A few compounds have exhibited as much as one percent carryover by liquid chromatography/mass spectrometry, so theoretically the reported value for the standards and samples could be one percent low. However, the measurement uncertainty for the method is 16 percent which is far greater than the theoretical loss from carryover. Any quantifiable concentration in the standards or spikes would be negligible in respect to carryover.

Issue 3:

The lab cannot find a possibility of carryover from one field sample to another from the analysis process. All samples received at the lab are handled per laboratory protocols which include precautions for preventing contamination.

Issue 4:

Carryover is usually not an issue with liquid chromatography. The system, as suggested by its name, has solvent running through it constantly. This action effectively is continuously rinsing the entire system while the instrument is operating. Carryover can be an issue when a very high concentration sample is analyzed followed by a lower concentration sample. However, the carryover issues currently seen are extremely low level detections when using ethyl acetate. Since carryover is generally not expected, the reviewers did not specifically look for it in the solvent blanks that were analyzed with each sample set.

Changes have been made to data review and to the analytical test sequences to alleviate any future possibility of carryover.

Issue 5:

No carryover was seen in any samples analyzed prior to May 2011 on this instrument. Carryover was only found to be present in samples analyzed from May 2011 through July 2011 and as this issue was brought to our attention, no false positives due to carryover were reported.

Through our investigations, we believe DEF was retained in some of the instruments sampling lines after the analysis of standards and spikes. By

analyzing many standards, the concentration of DEF became high enough that trace levels essentially bled into the next sample being analyzed. The instrument is also extremely sensitive for DEF which made it relatively easy to detect the trace levels reported.

The instrument manufacturer was contacted when lab personnel were unable to successfully eradicate DEF carryover from the internal sampling lines. The manufacturer eventually replaced several parts and flushed out the entire system. As of now, some carryover is still detected at lower levels in the solvent blanks prior to any samples analysis.

Issue 6:

The instrument in question has been used for other studies and data from May-July 2011 has been re-evaluated without evidence of carryover. As mentioned earlier, carryover is only occurring with samples prepared in ethyl acetate and only with specific analytes. There is no evidence of any carryover problems when methanol is used and the majority of analysis is done using methanol.

Issue 7:

The lab has implemented test procedures which include the analysis of additional solvent blanks after standards, spikes, and high concentration samples. The chemists and data reviewers have been notified to specifically look for any possible carryover effects.

The instrument manufacturer was not able to provide any information as to why the carryover was occurring, but agreed that the possibility of a "dead" space existed which could trap analytes, then slowly release trace amounts in subsequent injections. The instrument contains many small parts such as frits, connectors, and micro pump valves which could develop "dead" spots from constant motion. However, no definitive cause was determined.

I do not believe it is necessary to remove any of the analytes from the method. The possibility of carryover at trace levels is a known issue now and steps have been taken to prevent the reporting of any false positives.

Gas chromatography/ mass spectrometry would not provide any advantages to alleviating carryover with any of the analytes of interest. These analytes are more sensitive using liquid chromatography, so we would lose the ability to achieve the lower reporting limits. The instrument is already validated for these analytes and we currently do not have carryover problems. I believe it would be better to keep the analysis on the current instrument and be very vigilant in looking out for any carryover.

The data has been exhaustively reviewed by several chemists and there is no evidence to show the detections reported, other than DEF, were due to

carryover. The samples analyzed just prior to the samples with detections were completely free of any detectable analytes. The concentrations reported as trace are below our reporting levels, so there is no statistical confidence in the accuracy of the numbers reported. However, these trace detections had chromatographic data, including retention times, mass spectra, and mass data from two transitions which matches the reference standards.

To prevent the reporting of false positives in the future, the lab has taken steps to analyze more blanks after standards or samples with known amounts of target analytes. The analysts and data reviewers have been notified to specifically look for the possibility of carryover for all samples. Lastly, more frequent preventative maintenance measures of instrument parts will be done.

DPR's assistance in the prevention of reporting false positives would be greatly appreciated. The possibility for the chemistry staff to accidentally miss a questionable detection may still occasionally occur. If DPR staff notices an anomaly, it would be very advantages to notify the chemistry lab personnel as soon as possible. Data audits from your staff would be welcome and offer additional preventative measures.

Splitting samples with another lab and duplicate analyses are often difficult to assess. The levels being detected now in duplicate samples are not matching and we have no explanation for the differences. Using a second lab can provide some additional confidence in results, but also challenges if they are using different instrumentation and come up with different results. But if you choose to do this, we will do whatever is needed to accommodate the process.

The reporting of trace level analytes should be re-evaluated. The instrumentation being used is extremely sensitive, affording us the ability to detect into the low parts per trillion. Based on reference standards, we know these analytes are present and they are not carryover. The lab has been providing a concentration for these trace level detections as requested, but there is no scientific validity to these numbers.

We appreciate the opportunity to respond to your concerns. If you have questions or would like further discussion, please do not hesitate to contact me.

Sincerely,

Elaine Wong

Elaine Wong,
Environmental Program Manager I

Enclosure

Attachment A

Points 1 and 2: Field Blank samples collected on 8/24/11 and 12/28/11
#C00201-trace detection of malathion oxygen analog
#A00318-trace detection for malathion oxygen analog

Response: No carryover was seen in the solvent wash after the 5-point calibration curve and no solvent rinse was done after the spike. The area counts of the spike were one half that of the level 5 standard which had no carryover, so no carryover is anticipated from the spike. The field blank was the third sample in the sequence analyzed after the spike. The previous sample, a solvent blank, only had trace levels of malathion oxygen analog, so carryover would not be an issue. The retention time and ratio of the transitions was as expected for this analysis.

Point 3: Duplicate samples collected on 2/15/12
#C00353-trace detections for oxyfluorfen, S,S,S-tributylphosphorotrithioate (DEF), diuron, oryzalin, and simazine
#C00354: No trace detections

Response: DEF had 0.1% carryover in the solvent rinse after analyzing the 5-point calibration. 0.1% is determined by area counts from the carryover compared to the area counts from the highest concentration reference standard. A 0.01% carryover of DEF was detected after the spike in the solvent blank. The sample analyzed prior to C00353 showed very low level trace detections of diuron and simazine, any carryover would be unlikely and negligible. The 2 duplicate samples were analyzed two times with the same results. A trace level and extremely low trace level of oxyfluorfen was detected in samples C00353 and C00354 respectively by GC/MS analysis. The retention time and the spectra confirm the presence of oxyfluorfen in both samples.

Point 4: Duplicate samples collected on 2/09/12
#B00335-trace detections for Chlorpyrifos, Chlorpyrifos oxygen Analog, diuron, oryzalin, and simazine
#B00334-no trace detection

Response: Our records indicate that sample B00334 had no detectable levels of the analytes of interest. Sample B00335 was analyzed twice by both LC/MS and GC/MS with similar results. Trace detections of Chlorpyrifos, Chlorpyrifos oxygen Analog, diuron, oryzalin, and

simazine were confirmed. Very low trace level DEF was confirmed as carryover in this set of samples and was only seen in the solvent blank analyzed immediately following the calibration curve.

Point 5: Duplicate samples collected on 1/12/12
#B00308-0.56 µg detection for Chlorpyrifos, trace detections for Chlorpyrifos oxygen analog, diuron, and simazine
#B00314-No trace detections

Response: Just like the duplicate set collected on 2/9/2012, the samples were analyzed in the following order: A00330 only trace level of Dacthal and chlorpyrifos from GC/MS analysis: A11340 Trace level Chlorpyrifos OA from LC/MS and trace dacthal and chlorpyrifos from GC/MS: B00308 Trace level (but higher than in previous sample) Chlorpyrifos OA and trace diuron from LC/MS and reportable level of chlorpyrifos in the GC/MS analysis.: B00314 all N.D. There was no carryover in the GC/MS analysis. The spectra and the retention time verify the chlorpyrifos detection.

Point 6: Duplicate Samples collected on 9/6/11
#B00192: trace detections for Chlorpyrifos and Chlorpyrifos oxygen analog
#B00193: no trace detections

Response: These samples were analyzed in the following order: A00218 all N.D.: C00214 Only trace Chlorpyrifos OA (0.059) and trace Malathion OA (0.037): B00192 Trace chlorpyrifos OA (higher than in previous sample) and trace chlorpyrifos: B00193 all N.D. The spectra and retention time confirm the chlorpyrifos detection.

Possible modes of contamination within the laboratory have been discussed and are highly improbable. The levels found are from carryover due to analysis of standards and spikes just prior to the samples in question.

Department of Pesticide Regulation

Brian R. Leahy
Director

Edmund G. Brown Jr.
Governor

M E M O R A N D U M

TO: Elaine Wong, Branch Chief
California Department of Food and Agriculture
Center for Analytical Chemistry
Environmental Monitoring Section
3292 Meadowview Road
Sacramento, California 95832

FROM: Randy Segawa *Original signed by*
Environmental Program Manager
Environmental Monitoring Branch
916-324-4137

DATE: June 6, 2012

SUBJECT: FINAL ISSUES FOR S,S,S-TRIBUTYLPHOSPHOROTRITHIOATE TRACE DETECTIONS

Thank you for the information on the trace detections of S,S,S-tributylphosphorotrithioate for the air monitoring network (Study 257) provided in the memoranda dated March 8, 2012, and May 1, 2012 regarding the false positives due to instrument contamination caused by "carryover." While I still have some concerns about the false positives, you should continue the analyses as described in the May 1 memorandum.

Most of my concerns pertain to the estimated amount of carryover that can occur from one sample to the next. You estimated that S,S,S-tributylphosphorotrithioate had 0.01 – 0.1 percent carryover from one sample to the next. Therefore, the carryover from samples containing trace or low amounts would be undetectable in the following sample. I agree that the absolute amount of carryover may be small, but it may be higher than 0.1 percent. My conclusion is based on the odd results from the samples listed below.

- For field sample collected on 2/15/12
  #C00353: trace detection for S,S,S-tributylphosphorotrithioate

- For field blank sample collected on 8/24/11
  #C00201: trace detection for malathion oxygen analog

- For field blank sample collected on 12/28/11
  #A00318: trace detection for malathion oxygen analog

- For duplicate samples collected on 2/15/12
  #C00353: trace detections for oxyfluorfen, S,S,S-tributylphosphorotrithioate, diuron, oryzalin, and simazine
  #C00354: No trace detections

- For duplicate samples collected on 2/9/12
  #B00335: trace detections for chlorpyrifos, chlorpyrifos oxygen analog, diuron, oryzalin, and simazine
  #B00334: No trace detections

- For duplicate samples collected on 1/12/12
  #B00308: 0.56 ug detection for chlorpyrifos; trace detections for chlorpyrifos oxygen analog, diuron, and simazine
  #B00314: No trace detections

- For duplicate samples collected on 9/6/11
  #B00192: trace detections for chlorpyrifos, and chlorpyrifos oxygen analog
  #B00193: No trace detections

After further evaluation, you concluded that carryover did not occur in these samples and all of the detections are valid. From a field sampling perspective, several of these detections still appear to be unlikely.

- The Ripon detection of S,S,S-tributylphosphorotrithioate on February 15, 2012 is unlikely because no use of this pesticide occurred. This pesticide is used solely for cotton defoliation. The nearest cotton field is at least ten miles from the monitoring site, and applications only occur in the fall.

- The detection of malathion oxygen analog in two field blanks is unlikely because positive field blanks for any ambient air study has never occurred previously. Field staff do not handle pesticides during sampling and the monitoring sites are several hundred feet from the nearest pesticide applications. Moreover, it's unlikely to detect the oxygen analog breakdown product of malathion, but not the parent compound.

- For the four pairs of inconsistent duplicate samples, I noticed that each duplicate with no detections always followed the duplicate with trace detections in the analysis sequence. Additionally, the duplicate with trace detections was always analyzed just prior to a sample that had trace detections. In other words, the data would be more convincing if some of the samples with trace detections were analyzed after a sample with no detections.

While the Department of Pesticide Regulation (DPR) may consider these samples as false positives, you should not change your reports or conclusions. Even if DPR makes a final conclusion that these or other samples are false positives, DPR's report will include both opinions. Moreover, DPR will assume that the detections are valid for the purposes of evaluating health risk.

Based on the current analysis and data review procedures, you should continue to report all trace detections even if this may cause false positives and/or conflicting opinions about some detections. While this may be confusing and uncertain, I believe the need for transparency of the analysis and results outweighs the need for simplicity and clarity.

The potential for false positives at trace levels is not a major issue for the air monitoring network. However, this could be a major issue for other studies. Please inform Sue Peoples, of my staff, prior to using this instrument for other studies. No further actions, other than those currently planned, are needed at this time. Thank you for your assistance.

cc: Sue Peoples, DPR Staff Environmental Scientist

State of California

Memorandum

To : Randy Segawa
Environmental Program Manager
Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, CA 95812-4015

Date: July 16, 2012

Place: Sacramento

Phone: (916) 262-1434

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

Subject : **Response to Final Issues for S,S,S-Tributylphosphorotrithioate Trace Detections**

Thank you for your thoughtful correspondences, feedback, and providing the forum for discussing this issue. I am confident that following the new protocols put into effect, reporting of false positives will no longer be a concern.

Your concerns on the estimated amount of carryover are understandable. The percentages of carryover actually go from 0.01 to 1.0 percent. These numbers are calculations based on the total area counts of the peaks detected for the target analyte compared to the total peak area of the highest level reference standard for that analyte. The highest percentage of carryover for S,S,S - tributylphosphorotrithioate was 1.0 percent, where the trace detection had an area count of approximately 2000 and the reference peak area was 200,000. The lower trace amounts had areas of just under 100 counts. The chromatograms clearly show that the samples with reported trace detections, which have been identified as not being carryover, are accurately reported. Samples analyzed just prior to samples with trace detections had no quantifiable peaks of interest.

Although these findings appear to be unlikely from a field sampling perspective, a thorough and exhaustive laboratory investigation does not conclude the trace detections to be false. The lab cannot find an explanation for the detections. All the samples were analyzed more than once and some of the samples were analyzed from separate fractions in subsequent analyses.

The instrument in question has had a thorough evaluation and cleaning by an authorized engineer from the manufacturer. I am confident the instrument is in proper optimal operational condition and Sue Peoples will be informed of our intentions for use of this instrument in other studies.

The lab will continue to report all trace detections as you've requested. I also believe in transparency and therefore invite you and your staff to audit or review any of the data packages generated from your studies.

Sincerely,

Elaine Wong
Environmental Program Manager

APPENDIX C:
Derivation of Screening Levels

Health Evaluation Methods

No state or federal agency has established health standards for pesticides in air. Therefore, DPR developed health screening levels for these pesticides to place the results in a health-based context. Although not regulatory standards, these screening levels can be used in the process of evaluating the air monitoring results. A measured air level that is below the screening level for a given pesticide would not be considered to represent a significant health concern and would not generally undergo further evaluation, but also should not automatically be considered "safe" and could undergo further evaluation. By the same token, a measured level that is above the screening level would not necessarily indicate a significant health concern, but would indicate the need for a further and more refined evaluation. Significant exceedances of the screening levels could be of health concern and would indicate the need to explore the imposition of mitigation measures.

In 1996, Congress passed major pesticide food safety legislation. This legislation, the Food Quality Protection Act of 1996 (FQPA), made significant changes to the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Federal Food, Drug, and Cosmetic Act (FFDCA). Among other provisions, the FQPA requires U.S. EPA to review existing pesticide food tolerances (legal limits for pesticides in food) and to include an additional "safety factor" of up to 10-fold to account for uncertainty in data relative to children. U.S. EPA generally sets the factor at 1-fold, 3-fold, or 10-fold, depending on the completeness and reliability of the data available to assess pre- or post-natal toxicity and depending on the potential for pre- or post-natal effects of concern .This additional factor has become known as the "FQPA factor" or "FQPA safety factor." Although the U.S. EPA uses this factor for evaluating pesticide food tolerances and dietary risk, the factor is applied to all potential sources of exposure to children. They have also established the FQPA factors for pesticides in the course of preparing the RED for specific chemicals. DPR evaluated the results of this project by considering the "FQPA factor" in addition to the screening levels following discussions with the LAG and TAG. These recommendations were also available for public comment.

The uncertainty factor approach used in generating the screening levels implicitly assumes that there is a threshold below which the toxic effect will not occur. This approach is not appropriate for carcinogenic chemicals that have a non-threshold mechanism of action. For these chemicals, the chronic screening level does not include carcinogenic effects, and a cancer potency value is derived for that chemical. The carcinogenic risk of these compounds is evaluated using a low dose extrapolation (non-threshold mechanism). In such an approach, the risk of cancer from exposure to a chemical is determined from the cancer potency of the chemical and the human exposure to the chemical. For each monitored chemical that ahs carcinogenic effects, the cancer potency is presented along with the screening levels. Cancer potency is expressed in the units of $(mg/kg\text{-}day)^{-1}$. Cancer risk is expressed as a probability for the occurrence of cancer (e.g., 1 in 1,000,000 or 10^{-6}, 1 in 100,000 or 10^{-5}, etc). It is a standard default assumption that exposure to a carcinogen takes place over a lifetime, so the default respiratory rate for an adult is used (0.28 $m^3/kg/day$).

Screening Levels

Acephate

DPR completed a RCD in 2008, but air exposure was not a significant part of the overall exposure and reference concentrations were not set. U.S.EPA released an RED in 2006. In that document, the results of a 4-week rat inhalation study were specified to evaluate inhalation exposures of any duration. Rats were exposed 6 hours per day, and it is assumed they were exposed 5 days per week. The NOAEL was 1.064 mg/m^3 for brain cholinesterase inhibition. U.S.EPA assigned an FQPA value of 1X. These values lead to the calculation of acute, subchronic, and chronic NOAELs of 0.266, 0.19, and 0.19 mg/m^3, and human equivalent NOAELs of 1.20, 0.85, and 0.85 mg/m^3, respectively. Applying the uncertainty factor of 100X leads to the calculation of acute, subchronic, and chronic screening levels of 12.0, 8.5, and 8.5 ug/m^3, respectively.

Acrolein

The Department has initiated a risk assessment for acrolein and U.S. EPA has released an RED. Acrolein has extensive non-pesticidal (industrial) uses. In 2008, OEHHA modified its acute and chronic Reference Exposure Levels (RELs) for Acrolein as part of its Air Toxics Hot Spot program. These values have undergone external scientific peer review. OEHHA used eye irritation in a human exposure study to derive a 1-hour REL of 2.3 ug/m^3. The remaining RELs were set based on the occurrence of lesions of the respiratory epithelium in a rat inhalation study. In this study, rats were exposed by nose-only, 6 hours per day, 5 days per week, for 65 days. OEHHA set an 8-hour REL of 0.70 ug/m^3 and a chronic REL of 0.35 ug/m^3. Since the acute screening level is based on a 24-hour exposure, and the 8-hour and chronic RELs are so close, it is appropriate to use the chronic REL of 0.35 ug/m^3 as the acute (24 hour), subchronic, and chronic screening levels.

Arsenic

In 2008, OEHHA modified its acute and chronic Reference Exposure Levels (RELs) for Acrolein as part of its Air Toxics Hot Spot program. These values have undergone external scientific peer review. OEHHA used mouse developmental toxicity study to derive a 1-hour REL of 0.2 ug/m^3. OEHHA used decreased intellectual function in a study of 10-year old children consuming who drank arsenic contaminated drinking water to derive an 8-hour REL and chronic REL of 0.015 ug/m^3. This latter value will be used as the acute, subchronic, and chronic screening levels for arsenic.

Bensulide

U.SEPA released an RED in 2006. The RED specified the use of a NOAEL of 5.5 mg/kg for maternal plasma cholinesterase inhibition in a rat oral developmental toxicity study as the basis for assessing short-term inhalation. The RED specified the use of a NOAEL of 0.5 mg/kg for plasma cholinesterase inhibition in a chronic oral dog study as the basis for assessing intermediate-term inhalation. The RED did not address chronic or long-term inhalation; however, since the dog study was chronic, it would be appropriate for chronic inhalation. The RED specified an FQPA factor of 1X and an overall uncertainty factor of 100X. Applying uncertainty factor of 100 and the RfD to RfC conversion factor of 4.7

results in acute, subchronic, and chronic screening levels of 259, 24, and 24 ug/m^3 respectively.

Carbon disulfide

Sodium tetrathiocarbonate is applied to soil, but converts to carbon disulfide, sodium hydroxide, hydrogen sulfide, and sulfur in the soil. Carbon disulfide exerts the pesticidal activity in the soil. Hydrogen sulfide and carbon disulfide can move to the air and can then move offsite. Carbon disulfide is also generated by the breakdown of metam sodium into MITC (methyl isothiocyanate). This screening level is set for carbon disulfide.

Carbon disulfide has extensive not-pesticidal uses and exposure sources. OEHHA has set acute and chronic RELs for carbon disulfide as part of the air Toxic Hotspots Program. OEHHA set an acute 6-hour REL of 6,200 ug/m^3 based on a rat inhalation developmental toxicity study. In this study, rats were exposed for 6 hours a day for gestation days 6-20. The NOAEL was 620 mg/m^3 for decreased fetal body weight. OEHHA applied an uncertainty factor of 10 to address interspecies variability and a factor of 10 to address intraspecies variability. The REL does not incorporate a factor to compensate for differences in breathing rates between rats and people. The 6-hour REL of 6,200 ug/m^3 can be multiplied by 6/24 to derive a 24-hour screening level of 1,550 ug/m^3.

OEHHA set a chronic REL of 800 ug/m3 based on a study that evaluated people occupationally exposed (8-hour work day) to carbon disulfide. This study established an average LOAEL of 7.6 ppm for decreased nerve conduction. OEHHA used a benchmark concentration (BMC) and compensated for 24-hour exposure to establish a human equivalent concentration of 2.54 ppm. An uncertainty factor of 10 to account for intraspecies variation was applied, resulting in a REL of 0.254 ppm. OEHHA rounded this to 0.3 ppm (800 ug/m^3). 800 ug/m^3 were used as the subchronic and chronic screening levels.

Chlorothalonil

U.S. EPA completed an RED on chlorothalonil in 1999. The RED addressed inhalation for all time periods with a NOAEL of 2 mg/kg (kidney toxicity, forestomach ulcers) in a two-year oral rat study, assuming 100% absorption. Using this NOAEL and a combined uncertainty factor of 100 (a factor of 10 to address interspecies variability and a factor of 10 to address intraspecies variability) results in a screening level of 34 ug/m^3 for all time periods. U.S. EPA assigned a FQPA safety factor of 1X. U.S. EPA classified chlorothalonil as likely to be a human carcinogen by all routes of exposure (based on rat kidney tumors) and calculated a potency factor of 0.00766 $(mg/kg/day)^{-1}$. The RED uses both a potency factor and RfD approach for assessing carcinogenicity.

DPR completed a dietary RCD on chlorothalonil in 2004, which calculated a potency factor of 0.011 $(mg/kg/day)^{-1}$ for kidney tumors. This slightly higher potency factor was used in this analysis. Since the RCD is limited to dietary exposure, inhalation was not included. Inhalation exposure was evaluated in a comprehensive risk assessment (evaluates all routes of exposure and exposure scenarios) whose completion is pending

completion of the non-dietary exposure analysis. The completion of this risk assessment could result in changes to the above screening levels.

Chlorpyrifos

U.S. EPA released a finalized RED in 2006. The RED addressed short-term and intermediate-term inhalation using the same subchronic rat inhalation study. Rats were exposed 6 hours per day, 5 days per week. The highest dose level was 297 ug/m^3, and no effects were seen at any dose level, making 297 ug/m^3 a health protective NOAEL. For an acute screening level, the 297 ug/m^3 is adjusted by 6/24 to give a 24 hour NOAEL of 74 ug/m^3 and a screening level of 1.2 ug/m^3 (employs uncertainty factors of 10 each for inter and intraspecies uncertainty and corrects for differences in breathing rates). For the subchronic screening level, the value is adjusted by 5/7 to compensate for the 5 day out of 7-day exposure, leading to a screening level of 0.85 ug/m3. For chronic exposure, the IRED used a chronic oral dog study with a NOAEL 0.03 mg/kg for cholinesterase inhibition. This leads to an RfD of 0.0003 mg/kg and a screening level of 0.51 ug/m^3. U.S. EPA retained the FQPA safety factor of 10X.

U.S. EPA has assigned chlorpyrifos an "E" carcinogenicity classification, evidence of non-carcinogenicity.

Dacthal (Chlorthal dimethyl, DCPA)

U.S.EPA completed an RED on chlorthal dimethyl in 1998. Acute and subchronic toxicity were not addressed because they were not a concern (due to low toxicity). The RED used a NOAEL of 1.0 mg/kg for thyroid effects in a chronic oral rat study to assess chronic dietary exposure. An oral rabbit developmental toxicity study had a NOEL of 500 mg/kg (highest dose tested). This value will be used to assess acute exposure. A 90-day rat oral subchronic toxicity study had a NOEL of 10 mg/kg for liver effects, and this will be used to assess subchronic toxicity. The RED used an FQPA value of 1X and an overall uncertainty factor of 100X. Therefore, the acute, subchronic, and chronic NOELs to be used are 500, 10, and 1.0 mg/kg respectively. Applying the uncertainty factor of 100X and the RfD to RfC conversion factor of 4.7 results in acute, subchronic, and chronic screening levels of 23,500, 470, and 47 ug/m^3 respectively.

Cypermethrin

U.S. EPA released a revised RED in 2008. The RED stated that the NOAEL of 0.01 mg/L (10 mg/m^3) for body weight loss and salivation in a 21-day subchronic inhalation study in rats should be used to assess inhalation exposure scenarios of all durations. The RED also stated that an uncertainty factor of 3X should be applied to the above NOAEL to estimate a chronic NOAEL. In the study, exposure occurred 6 hours a day, 5 days a week. To estimate an acute 24-hour NOAEL, 10 mg/m^3 is adjusted by 6/24, resulting in a NOAEL of 2.5 mg/m^3. An adjustment of 5/7 results in a subchronic NOAEL of 1.8 mg/m^3 for exposure 7 days a week. The application of the 3X factor results in a chronic NOAEL of 0.6 mg/m^3. Applying a correction factor of 4.5 to the NOAELs will result in human equivalent acute, subchronic, and chronic NOAELs of 11.3, 8.1, and 2.7 mg/m^3, respectively. Applying an uncertainty factor of 10 for interspecies variation and 10 for

intraspecies variation results in acute, subchronic, and chronic screening levels of 113, 81, and 27 ug/m^3, respectively. U.S.EPA applied a FQPA safety factor of 1X.

U.S. EPA has designated cypermethrin as a "C" carcinogenicity classification (possible human carcinogen) but did not derive a cancer potency value.

Diazinon

The values for these screening levels were taken from a U.S. EPA IRED released in 2004. In this document, U.S. EPA determined that inhalation for all time periods should be evaluated using a 21-day rat inhalation study. The study used inhalation exposures of 6 hours per day, 7 days a week for 21 days. The LOAEL in this study is 0.1 ug/L (100 ug/m^3) for cholinesterase inhibition. U.S. EPA used a factor of 3 to derive a NOAEL from a LOAEL. Therefore, the NOAEL would be 33 ug/m^3. Normalizing to a 24-hour exposure results in a NOAEL of 8.33 ug/m^3 and a human equivalent NOAEL of 13.3 ug/m^3. This results in an acute, subchronic, and chronic screening level of 0.13 ug/m^3. U.S. EPA assigned a FQPA safety factor of 1X.

U.S. EPA has classified diazinon as "not likely to be carcinogenic to humans."

1,3-dichloropropene (1,3-D)

DPR has set RfCs for 1,3-D to support its ongoing control measures. The acute RfC of 200 ug/m^3 was calculated from the acute inhalation NOAEL of 10 ppm (6 hours per day) in rats, based on body weight reduction that is indicative of systemic effects. This RfC was calculated using a breathing rate for children of 0.46m^3/kg/day as opposed to the current default value of 0.59 m^3/kg/day. Using the value of 0.59 m^3/kg/day would result in a value of 160 ug/m^3. This latter value was used as the acute screening level.

The subchronic RfC of 150 ug/m^3 was calculated from the subchronic inhalation NOAEL of 10 ppm (6 hours per day, 5 days per week) in rats, based on degeneration and necrosis in the nasal epitheliium. This RfC was calculated using a breathing rate for children of 0.46m^3/kg/day as opposed to the current default value of 0.59 m^3/kg/day. Using the value of 0.59 m^3/kg/day would result in a value of 120 ug/m^3. This latter value was used as the subchronic screening level.

The chronic RfC of 150 ug/m^3 was calculated from the chronic inhalation NOAEL of 5 ppm (6 hours per day, 5 days per week) in mice, based hyperplasia and hypertrophy of the respiratory epithelium and hyperplasia of the urinary bladder mucosa. This RfC was calculated using a breathing rate for children of 0.46m^3/kg/day as opposed to the current default value of 0.59 m^3/kg/day. Using the value of 0.59 m^3/kg/day would result in a value of 120 ug/m^3. This latter value was used as the chronic screening level.

1,3-D is classified as a probable human carcinogen by U.S. EPA and is listed as a carcinogen under Proposition 65. DPR has calculated a cancer potency of 0.055 $(mg/kg/day)^{-1}$, based on the occurrence of broncheoalveolar adenomas observed in male mice in a chronic inhalation study.

Dichlorvos (DDVP)

At the time DPR developed the dichlorvos screening level for the Parlier project, the U.S. EPA had scheduled an RED for release. In 2001, U.S. EPA U.S. released a risk assessment for the RED. The RED has since been released. The risk assessment specified the use of a NOAEL of 0.1 mg/kg from an oral rabbit developmental toxicity study (maternal mortality, decreased weight gain, and cholinergic signs) to evaluate short-term inhalation. This NOAEL would result in an acute screening level of 1.7 ug/m^3. (U.S. EPA used an uncertainty factor of 100 X, excluding the FQPA factor, for all exposure periods.) The risk assessment specified the use of a NOAEL of 0.05 mg/kg from an oral dog chronic toxicity study (cholinesterase inhibition) to evaluate intermediate-term inhalation. This NOAEL would results in a subchronic screening level of 0.85 ug/m^3. The risk assessment specified the use of a NOAEL of 50 ug/m3 (inhibition of brain cholinesterase) in a chronic rat inhalation study. Exposure took place 23 hours a day, 7 days a week. The amortized NOAEL is 48 ug/mg^3, and the resulting screening level would be 0.77 ug/m^3. U.S. EPA assigned a FQPA factor of 3X and classified DDVP as having suggestive evidence of carcinogenicity.

DPR completed a RCD for DDVP in 1996, with two subsequent addenda. In the RCD, DPR evaluated acute inhalation exposure using the NOAEL of 1250 ug/m^3 (cholinergic signs) in a rabbit inhalation developmental toxicity study. Exposure took place 23 hours a day, 7 days a week. Amortizing the exposure to 24 hours results in a NOAEL of 1200 ug/m^3. Using this NOAEL and a rabbit breathing rate of 0.54 m^3/kg/day and a 100 X uncertainty factor results in an acute screening level of 11 ug/m^3. The same study, but with the lower NOAEL 250 ug/m3, was used to evaluate subchronic inhalation. This NOAEL would result in a subchronic screening level of 2.2 ug/m^3. The RCD used the same chronic inhalation study as was described for the U.S. EPA risk assessment, resulting in the chronic screening level of 0.77 ug/m^3. The DPR also developed a potency factor of 0.35 $(mg/kg/day)^{-1}$ based on leukemia in the rat. Since they were based on inhalation studies, the screening levels from the DPR RCD were used.

Dicofol

U.S. EPA completed a RED on dicofol in 1998. To evaluate short-term inhalation exposure, the RED uses a NOAEL of 4 mg/kg for increased abortions from an oral rabbit developmental toxicity study. This NOAEL results in an acute screening level of 68 ug/m^3. To evaluate intermediate-term inhalation exposure, the RED uses a NOAEL of 0.29 mg/kg for inhibition of ACTH release from a 90-day oral dog study. This NOAEL results in a subchronic screening level of 49 ug/m^3. To evaluate long-term inhalation, the RED uses a NOAEL of 0.12 mg/kg for release of ACTH release from a chronic oral dog study. This NOAEL results in a chronic screening level of 20 ug/m^3. U.S. EPA assigned dicofol a carcinogen classification of C, possible human carcinogen, but recommended an RfD approach for assessing risk. U.S. EPA assigned an FQPA factor of 3X.

Dimethoate

U.S. EPA completed an RED for Dimethoate in 2006. The RED specified that the results of a 21-day rat inhalation study on omethoate should be used to evaluate acute and subchronic inhalation exposure to Dimethoate. Omethoate is the more toxic oxygen

metabolic of dimethoate, so its use would be health protective. In the study, rats were exposed by nose 6 hours per day, 5 days per week, for 3 weeks. U.S. EPA used a benchmark dose extrapolation to determine a point of departure. The $BMCL_{10}$ for inhibition of brain cholinesterase calculated as 0.38 mg/m^3. This value is adjusted by 6/24 resulting in a 24 hour value of 0.095 mg/m^3. A further adjustment of 5/7 yields a subchronic value of 0.068 mg/m^3. An uncertainty factor of 10X can be used to estimate a chronic value of 0.0068 mg/m^3. Applying a correction factor of 4.5 to the $BMCL_{10}$s will result in human equivalent acute, subchronic, and chronic values of 0.43, 0.30, and 0.030 mg/m^3, respectively. Applying the conventional total uncertainty factor of 100 will result in acute, subchronic, and chronic screening levels of 4.3, 3.0, and 0.30 ug/m^3, respectively.

Diuron

U.S. EPA completed an RED on diuron in 1993. To evaluate short-term inhalation, the assessment uses a NOAEL 10 mg/kg for maternal toxicity in a rabbit developmental toxicity study. Applying this NOAEL, an uncertainty factor of 10 to address interspecies uncertainty, and a factor of 10 to address intraspecies uncertainty results in an acute screening level of 170 ug/m^3. To evaluate intermediate-term inhalation, the assessment uses a NOAEL 1.0 mg/kg for altered hematological values in the first 6 months of a chronic oral rat study. Applying this NOAEL, an uncertainty factor of 10 to address interspecies uncertainty, and a factor of 10 to address intraspecies uncertainty results in a subchronic screening level of 17 ug/m^3. To evaluate long-term inhalation, the assessment uses a LOAEL 1.0 mg/kg for altered hematological values in the same chronic oral rat study. U.S. EPA applied an uncertainty factor of 3 to estimate a NOAEL of 0.33 mg/kg. Applying this NOAEL, an uncertainty factor of 10 to address interspecies uncertainty, and a factor of 10 to address intraspecies uncertainty results in a subchronic screening level of 5.7 ug/m^3. U.S. EPA classified diuron as a likely human carcinogen (based on bladder and kidney tumors in rats and mammary tumors in mice) and derived a potency value of 0.0191 (mg/kg/day)$^{-1}$. U.S. EPA assigned an FQPA factor of 1X.

Endosulfan

DPR completed a risk assessment on endosulfan in 2008 under the Toxic Air Contaminant program. A 21-day rat inhalation study (nose only, 6 hours per day) was used as the basis for evaluating acute, subchronic, and chronic inhalation. Toxic effects in this study included various clinical signs of neurotoxicity and other signs of ill health (e.g. decreased body weight and food consumption). Using this study, the risk assessment established acute, subchronic, and chronic RfCs of 3.3, 3.3, and 0.33 ug/m^3, respectively. These values will be used as the corresponding screening levels.

EPTC

U.S. EPA completed an RED on EPTC in 1998. DPR has completed a RCD on EPTC. To evaluate short-term exposures, the RED used a NOAEL of 58 mg/m^3 for myocardial degeneration (heart muscle damage) from a 90-day rat inhalation study with exposure 6 hours per day, 5 days peer week. This NOAEL results in an acute screening level of 230 ug/m^3. To evaluate intermediate-term exposures, the RED used the same study. For exposures of less than 21 days, the RED used the above NOAEL, which results in a

subchronic screening level of 170 ug/m3. For intermediate-term exposures greater than 21 days, the RED used the same study, but a NOAEL of 8.3 mg/m^3 for clinical signs. This NOAEL results in a subchronic screening level of 24 ug/m^3. The RED did not select a value for evaluating long-term inhalation. The DPR RCD used an estimated NOAEL of 0.5 mg/kg/day for neuromuscular degeneration from a two-year oral rat study. This NOAEL converts to a chronic screening level of 8.5 ug/m^3. U.S. EPA has classified EPTC as not likely to be carcinogenic to humans. U.S. EPA assigned a FQPA factor of 10X.

Iprodione

An RED was completed on iprodione in 1998. The RED specified the use of a NOAEL of 20 mg/kg for developmental effects in a rat oral developmental toxicity study as the basis for assessing short-term inhalation. The RED specified the use of a NOAEL of 6.1 mg/kg for histopathological lesions in the male reproductive system and adrenal effects in males and females in a chronic oral rat study as the basis for assessing intermediate-term inhalation. The RED did not address chronic or long-term inhalation; however, since the rat study was chronic, it would be appropriate also for chronic inhalation. The RED specified an FQPA factor of 3X and an overall uncertainty factor of 100X. Applying uncertainty factor of 300X (includes the FQPA factor) and the RfD to RfC conversion factor of 4.7 results in acute, subchronic, and chronic screening levels of 313, 95.6, and 95.6 ug/m^3 respectively. U.S.EPA has classified iprodione as a likely human carcinogen with a potency factor of 4.39×10^{-2} (mg/kg/day)$^{-1}$.

Malathion

U.S. EPA released a revised RED on Malathion in 2009. Inhalation exposure was evaluated based on the results of a 90-day rat inhalation study in which rats were exposed 6 hours per day, 5 days per week. The lowest dose in the study, 100 mg/m^3, was a LOAEL based on histopathological effects in the respiratory epithelium, and a NOEL for plasma and RBC cholinesterase inhibition. U.S. EPA recommended the use of this study to evaluate short term and intermediate term inhalation exposure and used a factor of 10 to derive an estimated NOAEL of 10 mg/m^3 for the histopathological effects. Using this derived NOAEL, adjusting for the 6-hour per day exposure results in an acute NOEL of 2.5 mg/m^3. Adjusting for exposure 5 days per week will result in a subchronic NOEL of 1.79 mg/m^3. The RED did not have an evaluation of chronic inhalation. One approach would be to apply an additional uncertainty factor of 10X to the subchronic NOEL for a chronic NOEL of 0.179 mg/m^3. Applying the correction factor of 4.5 to the NOAELs will result in human equivalent acute, subchronic, and chronic NOAELs of 11.25, 8.06, and 0.81 mg/m^3, respectively. Applying an uncertainty factor of 10 for interspecies variation and 10 for intraspecies variation results in acute, subchronic, and chronic screening levels of 112.5, 80.6, and 8.1 ug/m^3, respectively. U.S.EPA applied a FQPA safety factor of 1X.

Metam Sodium/MITC

While metam sodium is the active ingredient that is applied in agricultural settings, it converts to fumigant methyl isothiocyanate (MITC), which moves into the ambient air. Therefore, screening levels are set for MITC. DPR has completed a RCD on metam

sodium and MITC. The RCD has undergone scientific peer review and has been accepted by the SRP. RELs were set in the RCD and reviewed by the SRP. DPR calculated an acute REL of 22 ppb (66 ug/m^3) based on eye irritation in a study of human volunteers. DPR set a subchronic REL of 1 ppb (3 ug/m^3) based on nasal epithelial atrophy in rat subchronic inhalation study. DPR set a chronic REL of 0.1 ppb (0.3 ug/m^3) based on the same subchronic rat study, but employing an uncertainty factor of 10X to address the uncertainty of using a subchronic value for chronic exposure. While metam sodium is classified by U.S. EPA as a probable human carcinogen, U.S. EPA has categorized MITC as having insufficient data for carcinogenicity classification. In the RCD, DPR concluded that the data were not sufficient to support a quantitative assessment of carcinogenicity. U.S. EPA did not assign a FQPA factor to MITC. The above RELs were used as the screening levels.

Methidathion

DPR completed a risk assessment of methidathion in 2007 as part of the Toxic Air Contaminant process. The assessment set RfCs for the acute, subchronic, and chronic timeframes. A NOEL of 0.18 mg/kg in a 90-day oral rat study for brain cholinesterase inhibition after 2 weeks was used as the basis for an acute RfC of 3.1 ug/m^3. This same value was used for the subchronic RfC. A NOEL of 0.15 mg/kg for liver effects in a 1-year oral dog study was used as the basis for a chronic RfC of 2.5 ug/m^3. U.S.EPA assigned an FQPA value of 1X and classified methidathion as a possible human carcinogen.

Methyl Bromide

DPR has completed an RCD for methyl bromide, which has undergone formal external peer review. RELs were set in the RCD. DPR calculated an acute REL of 210 ppb (820 ug/m^3) based on developmental effects (NOAEL of 40 ppm) in a rabbit developmental toxicity study. DPR calculated an REL of 9 ppb (35 ug/m^3) based on neurotoxic effects in a subchronic dog inhalation study designed to evaluate neurotoxicity. DPR calculated a chronic REL of 1 ppb (3.9 ug/m^3) based on nasal epithelial hyperplasia and degeneration in a chronic rat inhalation study. U.S. EPA has classified methyl bromide as not likely to be carcinogenic to humans. U.S. EPA assigned a FQPA factor of 1X.

Metolachlor

U.S. EPA issued a Tolerance Reassessment Decision (TRED) on metolachlor and s-metolachlor in 2002. The TRED was based on a report of the U.S. EPA Hazard Identification Assessment Review Committee (HIARC) released in 2001. In this report, U.S. EPA specified the use of the NOAEL of 50 mg/kg (for clinical signs, decreased body weight gain, and decreased food consumption) in an oral rat developmental toxicity study with s-metolachlor, for assessing short-term inhalation exposure. U.S. EPA specified the use of the NOAEL of 8.8 mg/kg (for decreased body weight gain) in an oral dog subchronic toxicity study, for assessing intermediate-term inhalation exposure. U.S. EPA specified the use of the NOAEL of 9.7 mg/kg (for decreased body weight gain) in an oral chronic dog study with metolachlor for assessing long-term inhalation exposure. In all cases, U.S. EPA specified the use of a total uncertainty factor of 100X. This would result in acute, subchronic, and chronic screening levels of 85 ug/m^3, 15 ug/m^3, and 16

ug/m^3, respectively. Since the subchronic screening level is slightly lower than the chronic screening level, it was used for both subchronic and chronic. U.S. EPA has classified metolachlor as a C, possible human, carcinogen, but has specified a non-linear MOE approach. U.S. EPA assigned a FQPA factor of 1X.

Naled (Dichlorvos/DDVP)
DPR completed a RCD on Naled in 1999 and an addendum in 2001. In the RCD, acute exposure, including inhalation, was evaluated using an estimated NOAEL of 2.5 mg/kg, based on neurotoxic effects in an oral rat Functional Observational Battery study. Subchronic exposure was evaluated using a NOAEL of 2.5 mg/kg (in terms of absorbed dose and amortized for daily exposure) for cholinesterase inhibition in a subchronic dermal rat study. Chronic exposure was evaluated using a NOAEL of 0.2 mg/kg for brain cholinesterase inhibition in a chronic rat study. This would result in acute, subchronic, and chronic screening levels of 43 ug/m^3, 43 ug/m^3, and 3.4 ug/m^3, respectively.

In 2002, U.S. EPA released an RED on naled. In the RED, U.S. EPA used a NOAEL of 0.23 mg/m^3 for cholinesterase inhibition from a 13-week rat inhalation study to evaluate inhalation exposure of any duration. In this study, exposure took place 6 hours per day, 5 days per week. Adjusting for the 6-hour exposure and breathing rate differences results in a human equivalent NOAEL of 92 ug/m^3. Applying an uncertainty factor of 100 results in an acute screening level of 0.92 ug/m^3. Adjusting for exposures 5 days per week results in subchronic and chronic screening levels of 0.65 ug/m^3. U.S. EPA assigned a cancer classification of E, evidence of non-carcinogenicity and assigned a FQPA factor of 1X. Since the screening levels based on the RED are derived from an inhalation study, they were used here.

Norflurazon
U.S. EPA completed an RED in 1996 and a TRED in 2002. Neither document addressed inhalation exposure; therefore, the screening levels are set based on oral toxicity values. The TRED evaluated acute dietary exposure using the NOAEL of 10 mg/kg/day for increased skeletal variations in an oral rabbit developmental toxicity study. Using this NOAEL and a combined uncertainty factor of 100 results in an acute screening level of 170 ug/m^3. The TRED evaluated chronic dietary exposure using the NOAEL of 1.5 mg/kg/day for liver toxicity in a 6-month oral dog study. Using this NOAEL and a combined uncertainty factor of 100 results in chronic screening level of 26 ug/m^3. The TRED did not evaluate intermediate-term or subchronic exposure; therefore, the chronic screening level of 26 ug/m^3 was also used as the subchronic screening level. U.S. EPA has classified norflurazon as a possible human carcinogen based on liver tumors, but did not recommend a quantitative risk assessment. U.S. EPA assigned an FQPA factor of 3X only for acute exposure of females 13-50 years of age, while assigning an FQPA factor of 1X for all other acute exposures and all chronic exposures.

Oryzalin
U.S. EPA completed an RED in 1994 and published a risk assessment in 2003, which will form the basis for a TRED. In the risk assessment, U.S. EPA specified evaluating short-term inhalation using the NOAEL of 25 mg/kg (maternal toxicity in an oral rabbit

developmental toxicity study) and applying an uncertainty factor of 100X. This would result in an acute screening level of 420 ug/m^3. U.S. EPA specified evaluating intermediate-term and long-term inhalation using the NOAEL of 13.82 mg/kg (decreased weight gain, hematological effects, and thyroid effects in a chronic rat feeding study) and applying an uncertainty factor of 100X. This would result in a subchronic and chronic screening level of 230 ug/m^3. U.S. EPA classified oryzalin as likely to be carcinogenic to humans and assigned a slope factor of 0.00779 $(mg/kg/day)^{-1}$. U.S. EPA assigned an FQPA factor of 1X.

Oxydemeton-methyl

An RED was completed on oxydemeton-methyl in 2006. The RED and the supporting risk assessment specified the use of the results of a 4-hour acute inhalation study (with no NOEL) as the basis for assessing inhalation exposures of all durations. This could be viewed as an over-extrapolation. Therefore, the studies used by the RED to assess acute and chronic dietary exposure will be used as the basis for evaluating inhalation exposures of differing duration. A LOAEL of 2.5 for cholinesterase inhibition in a rat oral acute neurotoxicity study was used as the basis for assessing acute dietary exposure. The RED used an uncertainty factor of 3X to account for the use of a LOEL, for a total uncertainty factor of 300X. A NOAEL of 0.013 mg/kg for decreased brain cholinesterase in a 1-year oral dog study was used, along with an uncertainty factor of 100X, as the basis for assessing and chronic exposure. This value will also be used to assess subchronic exposure. The RED specified an FQPA factor of 1X. Applying the uncertainty factors and the RfD to RfC conversion factor of 4.7 results in acute, subchronic, and chronic screening levels of 39.2, 0.61, and 0.61 ug/m^3 respectively.

Oxyfluorfen

U.S. EPA completed an RED in 2002. In the RED, U.S. EPA specified evaluating short-term inhalation using the NOAEL of 30 mg/kg (maternal toxicity in an oral rabbit developmental toxicity study) and applying an uncertainty factor of 100X. This would result in an acute screening level of 510 ug/m^3. U.S. EPA specified evaluating intermediate-term inhalation using the LOAEL of 32 mg/kg (liver toxicity a subchronic mouse feeding study), and applied an uncertainty factor of 3X to derive a NOAEL of 10.67 mg/kg. Applying an uncertainty factor of 100X results in a subchronic screening level of 180 ug/m^3. U.S. EPA specified evaluating long-term inhalation using the NOAEL of 3.0 mg/kg (liver toxicity in chronic dog and mouse studies). Applying an uncertainty factor of 100X would result in a chronic screening level of 51 ug/m^3. U.S. EPA classified oxyfluorfen as a possible human carcinogen based on liver tumors in mice and assigned a slope factor of 0.0732 $(mg/kg/day)^{-1}$. U.S. EPA assigned an FQPA factor of 1X.

Permethrin

U.S. EPA completed an RED on permethrin in 2005. In the RED, U.S. EPA specified using the NOAEL of 42 mg/m^3 (neurotoxicity in a 15 day rat inhalation study) to evaluate short-term, intermediate-term, and long term-inhalation exposure. U.S. EPA applied an uncertainty factor of 100X. The study exposed animals 6 hours a day for an average of 3.75 days a week. Adjusting for exposure for 24 hours and differences in

breathing rates results in a human equivalent acute NOAEL of 16.8 mg/m^3. Applying the uncertainty factor of 100X results in an acute screening level of 168 ug/m^3. Adjusting this value for exposure 3.75 days per week results in subchronic and chronic screening levels of 90 ug/m^3. U.S. EPA classified permethrin as likely to be carcinogenic to humans based on lung tumors in mice and derived a slope factor of 0.00957 (mg/kg/day)$^{-1}$. U.S. EPA assigned an FQPA factor of 1X.

Phosmet

U.S. EPA completed an IRED for Phosmet in 2001. In the IRED and supporting risk assessment, U.S. EPA specified evaluating short-term inhalation using the NOAEL of 4.5 mg/kg (cholinesterase inhibition an acute rat oral neurotoxicity study) and applying an uncertainty factor of 100X. This would result in an acute screening level of 77 ug/m^3. U.S. EPA specified evaluating intermediate-term inhalation using the NOAEL of 1.5 mg/kg (cholinesterase inhibition in an oral subchronic rat neurotoxicity study) and applying an uncertainty factor of 100X. This would result in a subchronic screening level of 26 ug/m^3. U.S. EPA specified evaluating long-term inhalation using the NOAEL of 1.1 mg/kg (cholinesterase inhibition in an oral rat chronic toxicity study) and applying an uncertainty factor of 100X. This would result in a chronic screening level of 18 ug/m^3. U.S. EPA classified phosmet as having suggestive evidence of carcinogenicity, but not sufficient to assess human carcinogenic potential. U.S. EPA assigned an FQPA factor of 1X.

Propargite

U.S. EPA completed an RED on propargite in 2001. In the RED, U.S. EPA used a LOAEL of 310 mg/m^3 (mortality in a 4-hour rat inhalation study) to evaluate short-term, intermediate term, and long-term inhalation. The RED specified a total uncertainty factor of 1000X. This included a 10X factor due to the lack of a NOAEL, the severity of effects at the lowest dose tested, and the 4-hour exposure duration. Adjusting for differences in human and rat breathing rates and using this 1000X uncertainty factor would result in a screening level of 496 ug/m^3 for all timeframes. U.S. EPA has classified propargite as a probable human carcinogen based on intestinal tumors in rats. The RED specified a cancer potency factor of 0.0033 (mg/kg/day)$^{-1}$. U.S. EPA assigned an FQPA factor of 1X.

DPR completed an RCD on propargite in 2004. In the RCD, DPR derived an acute RfC of 14 ug/m^3 based on maternal toxicity at 2 mg/kg in a rabbit developmental, an oral absorption rate of 40%, and an uncertainty factor of 100. DPR derived a chronic RfC of 26 ug/m3 based decreased body weights and decreased food consumption at 3.8 mg/kg in a chronic rat study, an oral absorption rate of 40%, and an uncertainty factor of 100. The seeming incongruity of a chronic NOAEL higher than the acute NOAEL is probably the result of dose selection. Since the current process is intended to develop screening levels, a conservative approach would be to use the lower acute value to examine all time periods. For propargite, the screening level of 14 ug/m^3, derived from the acute RfC was used for evaluating acute, subchronic, and chronic exposures. In the RCD, DPR calculated cancer potency values in a range of 0.0059 to 0.026 (mg/kg/day)$^{-1}$.

SSS-tributyltriphosphorotrithioate (DEF)

In 1999, DPR completed an RCD on DEF that was peer reviewed by the SRP. The RCD derived an acute and subchronic REL of 8.8 ug/m^3 based on cholinesterase inhibition and clinical signs in a 90-day rat inhalation study. Since DEF is not used year round, chronic inhalation exposure was not evaluated. DPR derived a carcinogenicity potency factor of 0.084 $(mg/kg/day)^{-1}$. In a 1999 IRED, U.S. EPA specified the use of the same study to evaluate short-term and intermediate term exposure. The RED also did not evaluate long-term inhalation exposure. U.S. EPA classified DEF as a likely high dose/not likely low dose carcinogen and recommended that a potency factor not be calculated. U.S. EPA retained the FQPA factor of 10X.

Simazine

U.S. EPA released an RED on simazine in 2006. The RED evaluated short-term inhalation using a NOAEL of 6.25 mg/kg from a 28-day oral pubertal study in rats. This NOAEL results in an acute screening level of 110 ug/m^3. The RED recommended evaluating intermediate-term and long-term inhalation exposure using a NOAEL of 1.8 mg/kg from an oral 6-month luteinizing hormone surge study in rats. This NOAEL results in both subchronic and chronic screening levels of 31 ug/m^3. U.S.EPA classified simazine as not likely to be carcinogenic to humans and assigned an FQPA factor of 3X.

Trifluralin

U.S. EPA completed an IRED on trifluralin in 2004. The IRED assessed short-term inhalation was assessed using a NOAEL of 300 mg/m^3 for methemoglobinemia and clinical signs in a 30-day rat inhalation study in which exposure took place 6 hours a day, 5 days a week. The amortized 24-hour NOAEL would be 75 mg/m^3. Adjusting for differences in rat and human breathing rats and applying a total uncertainty factor of 100X results in an acute screening level of 1,200 ug/m^3. Intermediate-term inhalation was assessed using a NOAEL of 10 mg/kg for kidney and urine chemistry effects in an oral rat urinalysis study. This would convert to a subchronic screening level of 170 ug/m^3. Long-term inhalation was assessed using a NOAEL of 2.4 mg/kg for decreased body weight, decreased red blood cells, and other hematological effects in an oral chronic dog study. This would convert to a chronic screening level of 41 ug/m^3. U.S. EPA classified trifluralin as a C, possible human carcinogen and derived a cancer potency value of 0.0058 $(mg/kg/day)^{-1}$. U.S. EPA assigned an FQPA factor of 1X.

APPENDIX D:
Responses to Comments on the Draft - Air Monitoring Network Results for 2011
Volume 1

APPENDIX D:

Reponses to Comments on the
AIR MONITORING NETWORK RESULTS FOR 2011
VOLUME 1

Comment Number	Comment	Response	Action
1.	**Sampling days –** The third paragraph of the summary states that "24-hour samples were collected every week at each of the 3 sites." We suggest clarifying this sentence to indicate that one 24-hour sample was collected each week at each of the three sites.	Sentence was modified to read as follows: One 24-hour sample was collected each week at each of the three sites.	*Incorporated.*
2.	**Acrolein data –** The fourth paragraph of the summary notes that "acrolein detections are consistent with statewide monitoring results from the Air Resources Board." Since the acrolein detections are attributed to automobile emissions and not to pesticidal use of acrolein, we recommend removing the sentence from the summary. In the body of the report when referring to acrolein data, if pesticide use data verifies that there were no pesticidal uses of acrolein near the three monitoring sites, we suggest inserting the following sentence: "(Note: ARB has reclassified their air monitoring results for acrolein as "unverified" due to concerns about analytical standards used to calibrate the analytical instruments.)"	Sentence in the fourth paragraph of the summary was removed and the suggested note was inserted on page 13 of the report.	*Suggested changes to the report were made.*
3.	**Description of towns –** The introduction describes the towns selected for monitoring. In those descriptions, the area of Shafter is listed as 28 square miles with a population of 16,988, while the area of Salinas is listed as 23.2 square miles with a population of 150,441. We suggest that you verify that the area of Shafter is actually larger than Salinas.	The original number of Shafter area of 28 square miles was erroneous. The actual Shafter city area is 18 square miles. The Shafter description paragraph was updated to reflect the correct area value. Additionally, the areas of Salinas and Ripon were also updated to reflect their actual values of 19 and 4.2 square miles, respectively.	*Reported city areas were replaced with correct city areas*

Comment Number	Comment	Response	Action
4.	**Laboratory audits –** The data validation/quality assurance portion of the report describes audits of three laboratories: the CDFA Center for Analytical Chemistry, the ARB Organic Laboratory, and the ARB Inorganic Laboratory. The report summarizes the recommendations of the audits. We suggest clarifying if the recommendations apply to all three laboratories or just an individual laboratory.	The data validation/quality assurance portion of the report addressees audit recommendations made specific to CDFA procedures. Therefore, the paragraph on page 45 has been edited as follows: "The QA team recommended that analytical standards used by CDFA for quantitation of sample results should have current certification dates and be verified against a second source where possible. They also recommended that development and implementation of a procedure for the preparation of blind spikes for the VOC analysis and the development of specific procedure/policy for handling the duplicate analyses be created by CDFA personnel."	*Suggested changes to the report were made.*
5.	**Presentation of Data –** In Table 4 results are reported in terms of percent of samples with detections of a given pesticide but it would have been more helpful if these were divided up by site. For example, of the 40+ samples at a given site, how many had trace and quantifiable detections for each individual pesticide monitored. Most or all of the pesticides listed on page 12 as EPA B2 carcinogens are also chemicals on the Proposition 65 list for cancer.	The suggested tables were added. Potential health effects are described in Appendix C of the report.	*Suggested changes to the report were made.*
6.	**Disadvantages of sampling once a week revealed in monitoring results –** In theory, sampling on a random day once a week should provide a representative sample. However, when the sampler malfunctions, as happened in Ripon several times, a significant amount of data is lost. In addition, the Department is now not sure they have an adequate number of data points to calculate cancer risk estimates. At the most recent PREC meeting, Randy Segawa said that the Department was considering doing a cancer risk estimate for 1,3 D but that with 5 detections it's hard to do the calculation or decide how to handle the samples with no detection. To more accurately determine levels in the air when pesticides are used, a focused effort at peak times would give more information than picking 1 day randomly per week. When the PREC reviewed plans for the Air Monitoring Network, the ARB recommended sampling more frequently for specific pesticides during the times of the year when those pesticides are used in the area. We urge the Department to reconsider this approach.	Current departmental budgetary issues require that we only sample once per week. More frequent sampling cannot be done without reducing the number of sites or pesticides monitored. DPR based the current collection plan of one 24-hour sample at each of the three sites on its evaluation of results from the department's one-year study in Parlier that included air monitoring at three locations, three days each week. The Parlier data indicated that monitoring a single location once a week will provide adequate data to estimate long-term concentrations. Therefore additional sampling dates will be not be included in the air monitoring network's future schedule.	*No changes to the report are needed*

Comment Number	Comment	Response	Action
7.	**Salinas Site Concerns –** During the site selection process the Air Resources Board expressed reservations about the Salinas airport site because it is located on the outskirts of Salinas, some distance from most crop land and while night time winds blow towards the airport from Salinas, day-time winds blow in from the bay diluting pesticide air levels. The residential areas of Salinas are also closer to crop land than the airport. The Department acknowledged that the airport was not their first choice for a Salinas site either. We note that only trace levels of most of the non-fumigant pesticides sampled for were measured at the Salinas site during 2011 despite heavy use of many of these pesticides on crops grown in the Salinas valley. Air levels of methyl bromide were significant but substantially lower than levels measured by ARB at the Santa Maria site even though level of use of methyl bromide is similar in the two areas. We urge the Department to consider relocating the Salinas site either to a more centrally located Salinas site or possibly south to Chular, Gonzales or Greenfield, communities previously identified as potential monitoring sites, to the Santa Maria site operated with ARB, or north to supplement sampling at the Watsonville school where some sampling is already being conducted in cooperation with the ARB. Due to the combination of past reservations about selection of this site and sampling results which seem out of synch with Salinas Valley pesticide use patterns we conclude it would be a waste of further time and resources to keep using this site until the 2011 pesticide use data can be analyzed.	While the current Salinas site location is not centrally located, it is close enough to the Salinas crop land and residential housing to provide accurate representation of Salinas' day-time and night-time air concentrations. Additionally, due to a legal agreement between DPR and U.S. EPA, the Department is required to continue methyl bromide ambient monitoring at the current Salinas sampling location, along with the new Watsonville sampling site, until the end of 2013. At which time decisions regarding possible site removal, site addition, or change of location will be fully explored. Higher use of fumigants occur north and west of Salinas (e.g., Watsonville), and higher use of nonfumigants occurs south of Salinas (e.g., Chular and Gonzales). No single site in Monterey County can be located in the area of highest use for both fumigants and nonfumigants. If monitoring continues in Monterey County after 2013, DPR will consider splitting the sampling, with one site for fumigants in the north and one site for nonfumigants in the south.	*No changes to the report are needed*

Comment Number	Comment	Response	Action
8.	**Concerns regarding possible sampling and analytical issues –** We are concerned that the Quantitation Limit for chloropicrin of 2, 778 ng/m^3 is higher than either the Sub-Chronic or Chronic Screening Levels and 12.5 times higher than the Detection Limit. It also seems strange that there were non unquantifiable detections of chloropicrin and only 3 quantifiable detections, all at the Salinas site. We are concerned that the false positive results for DEF and now possibly methyl iodide raise questions about lab procedures but we have no expertise in this area. More blank samples between test samples may be advisable. We note that there was a large discrepancy in one pair of MITC duplicate samples. Average field spike percent recoveries were quite low for some pesticides and no ranges or standard deviations are reported. The response to the ARB audit discusses steps taken to address low recoveries with iprodione and MITC and chloropicrin only. The ARB audit on page 14 highlights some sampling problems including lack of an SOP for VOC sampling, storage of SUMMA canisters in refrigerator, incomplete chain of custody sheets, temperature of the storage refrigerator dropping below the accepted range, and tree possibly too close to sampling inlet at Ripon site.	Current detection and quantification limits were set by our laboratory personnel and the levels set are the best achievable values based on the current methods and equipment that the lab possesses. Therefore, reducing a chemical's current detection or screening levels may entail a new method development and possibly purchase newer equipment. Since new method development could take over a year to complete and could delay the study, the latter cannot possibly be undertaken at the current time. We are not opposed to looking into lowering the various limit levels for all or some of the target chemicals in the future if a new method is achieved. Page 45 – 49 of the report detail how the CDFA laboratory and DPR staff are working into resolving some of the analytical issues that were presented during the sampling and sample analysis. Additionally, Appendix B shows a concerted effort to identify and prevent future carryover issues. To minimize possible issues, additional blank samples are being inserted between test samples and new procedures are being examined. Issues raised in the ARB audit regarding lack of some SOPs, sample storage, Chains or Custody, and storage temperatures have been fully addressed and corrected.	*No changes to the report are needed*
9.	**Methyl Bromide –** DPR's seasonal regulatory limit for methyl bromide of 19,400 ng/m^3 (5 ppb) is not considered adequately health protective by OEHHA. OEHHA supports a seasonal or sub-chronic limit of 3,880 ng/m^3 (1 ppb) to protect children. This was exceeded at the Salinas site as well as the Santa Maria and Oxnard sites.	DPR will continue to use the subchronic value of 5 ppb derived in the risk assessment of methyl bromide and considered to be adequately health protective by its toxicologists, and is the goal established by DPR management. A footnote has been added to Table 10 to indicate that this is a regulatory goal specified by DPR.	*No changes to the report are needed*

Comment Number	Comment	Response	Action
10.	**Chloropicrin –** The 1-day acute screening level for chloropicrin of 491,000 ng/m^3 (73 ppb) is the regulatory level set by DPR management in the Chloropicrin Risk Management Directive. In contrast, the 24 hour acute screening level for children derived by DPR toxicologists in the TAC report is about 80 fold lower- 6,180 ng/m^3 (0.92 ppb). The highest 24 hour concentration measured in Salinas, 3,926 ng/m3 was about 63% of the acute chloropicrin REL for children listed in the TAC report. The seasonal chloropicrin screening level used is the same as the level derived in the TAC report. It is concerning that the Salinas site reached 78.9% of the chloropicrin sub-chronic screening level and 64% of the Acute Screening Level derived in the TAC report because this site is located further from major areas of fumigant use than the main residential areas of Salinas. In the TAC report finalized by DPR in 2010, OEHHA, the SRP and DPR toxicologist all concluded that chloropicrin is highly potent carcinogen so a calculation of cancer risk should also be included for chloropicrin utilizing the Cancer Potency HEC of 2.2 (mg/kg/day)$^{-1}$ and RfC for cancer of 0.24 ppt derived in the TAC report.	The DPR Risk Management Directive "determined that the appropriate regulatory target level to restrict acute exposure to chloropicrin is 73 parts per billion (ppb) or 0.073 ppm averaged over an eight-hour period. A footnote has been added to Table 9 to indicate that this is the regulatory goal specified by DPR. This level is based on the evaluation of human studies by Cain in 2004, literature review, U.S. EPA's risk assessment, and DPR's RCD. Based on the human study by Cain, acute effects of eye irritation will not be expected at 73 ppb. According to the same study, 20 percent of the individuals reported some eye discomfort at 100 ppb, and 40 percent of the individuals reported increasing discomfort at 150 ppb. Since the level of discomfort was reported subjectively by individual scoring instead of direct clinical observation, it is difficult to ascertain dose levels at which the individuals experienced those effects." We share CRLA's concern and welcome their input regarding some of the measured chloropicrin air levels. Mitigation measures to address these concerns are under consideration. It is an overstatement to say that DPR toxicologists concluded that chloropicrin is a "highly potent carcinogen." DPR toxicologists presented several caveats in the document that pertain to the uncertainty of carcinogenicity.	*No changes to the report are needed*
11.	**Chlorpyrifos and Diazinon –** FQPA adjusted hazard quotients should be included in this report as they were in the Parlier report (at least in the draft I just looked at). PANNA has derived a chlorpyrifos Subchronic Screening Level for children of 170 ng/m^3, about 8 fold lower than the screening level of 850 ng/m^3 used in this draft repo1t.	The FQPA factor for diazinon is 1X. Chlorpyrifos is currently undergoing risk assessment at both USEPA and DPR, so it is possible that toxicity values will change based on those assessments. Until those documents are finalized, the current screening level will be maintained. EPA initially recommended the use of a 10X FQPA factor, but did not apply the factor in its most recent draft assessment. DPR commented that the FQPA factor should be retained and currently supports applying that factor. It may be appropriate to include hazard quotients both with and without the FQPA factor, as was done in the Parlier Report.	*No changes to the report are needed*

Comment Number	Comment	Response	Action
12.	**Risk Assessment Statements Outside of the Context of the Study Draft Report, Page 51 –** Page 51 contains the statement "*While the air concentrations are considered low, these pesticides had higher relative risk in comparison to the other AMN pesticides*." The pesticides referenced include the soil fumigants 1,3-dichloropropene, chloropicrin, methyl bromide and MITC. All of the air monitoring results for these pesticides were well below the DPR health screening guidelines for the specific pesticide. Moreover the Air Monitoring report is not a risk assessment for any specific pesticide, or an assessment of the comparative risk of monitored pesticides, but rather is an analysis of the potential presence of the listed pesticides in ambient air above selected screening levels. Therefore this statement and similar statements regarding risks are not within in the context of the study and should be removed from the report. These out-of-context statements serve no purpose and may confuse readers.	To avoid possible reader confusion and to eliminate context ambiguity, the statement previously located on page 51 was removed.	*Suggested changes to the report were made.*
13.	**Incorrect 4-Week Average for Chloropicrin Draft Report, Page 20 –** The second sentence of the text on this page states that the maximum 4-week concentration of chloropicrin was 3,930 ng/m^3. The correct value for the 4-week average is 1,810 ng/m^3 as shown on table 7, page 21.	Chloropicrin's maximum 4-week concentration was erroneously listed as 3,930 ng/m^3 on page 20 of report. Error has been corrected and new sentence reads as follows: The pesticide with the next highest subchronic exposure was chloropicrin, with a maximum 4-week concentration of 1,810 ng/m^3 or 79% of its screening level.	*Report was updated with correct value.*

Comment Number	Comment	Response	Action
14.	**Explanation of Non-Detect Samples –** In several places in the draft DPR does not adequately note and explain the impact of DPR's practice of (1) substituting a value of one-half of the Method Detection Limit (MDL) for samples with no detectable amount of the pesticide in question and (2) substituting the midpoint between the MDL and the Limit of Quantitation (LOQ) for trace samples. This practice produces an artificial screening level value that is treated as if it were an actual measured value. DPR's methodology is explained in the report; however the artificial nature of these values is not made clear each time the values are presented. Under the DPR methodology the mere fact of monitoring for a pesticide will create the artifact of the chemical being measured, even if it is not present. It is important that the reader understand that in some cases "% Screening Levels" are increased even where no measurable detections occurred. For example, no sample collected in Shafter and Ripon had detectable chloropicrin, yet the methodology results in an increase in screening levels for chloropicrin which were reported as 0.023% for acute exposure, 4.8% for 4-week exposure and 6.2% for chronic exposure. The CMTF urges DPR to stop using this approach for a monitoring study. At a minimum DPR should make clear that the values produced are not measured values and acknowledge the impacts of the approach on its percentage calculations.	The report's glossary fully explains on page ix the definition of a trace concentration: "Samples with concentrations above the minimum detection limit but below the LOQ can be identified as containing a *trace* amount but the concentration cannot be measured reliably. When calculating average concentrations or other statistics, DPR assumes that samples with a trace concentration have a concentration at the midpoint between the MDL and the LOQ. As with the MDL, the LOQ is a characteristic of both the method and the chemical. Different methods can have different LOQs limits for the same chemical. The same method can have different LOQs for different chemicals". A new section titled "Uncertainty of Air Concentrations - Treatment of ND and Trace Samples" on page 47 along with Table 32 on page 48 were added to the report. The highest 4-week rolling concentrations and overall average concentration for pesticides with at least one detectable concentration were calculated by using three different methods which treat samples with no detectable concentration and trace concentrations differently. Results show that replacing DPR's standard method with any of the two alternative methods tested does not affect the "% Screening Levels" by a large enough margin to alter the reports findings. Therefore, current DPR's standard method for treating samples with no detectable concentration and trace concentrations will remain the same.	*Some changes were made to the report*
15.	**Page 29, Appendix A Technical System Audit –** The Technical System Audit indicates on Table 1 that the analytical method detection limit and the quantitation limit for chloropicrin were not developed at the time of the audit. The validation for these methods should be provided in the report.	CDFA lab personnel performed a verification of chloropicrin method before the TSA audit took place, however no updated written method SOP was available for audit personnel to review. CDFA has finalized the SOP and the updated method is available on-line: (http://www.cdpr.ca.gov/docs/emon/pubs/anl_methds/methd_em_16.pdf) The MDL is 0.016 µg/sample and RL is 0.2 µg/sample.	*No changes to the report are needed*

Comment Number	Comment	Response	Action
16.	**Comparison of Air Monitoring Results with Pesticide Use and Weather Data is vital –** This report explains that the Department will compare detected air concentrations with pesticide use patterns as well as weather conditions once the 2011 pesticide use reports have been compiled and verified. We think this step is vital and that for the most part it is premature to draw conclusions about the significance of air monitoring results before this further analysis is conducted. The conclusion in the summary that these air monitoring results indicate that buffer zones, application method restrictions and use limits appear to have been effective at reducing fumigant exposures below levels of concern is premature without an analysis of weather patterns and levels of fumigant use in proximity to each site. It is also premature to consider dropping any pesticides from further monitoring until after a comparison is made with pesticide use patterns and a full year of data is available. In addition, since 2011 sampling was initiated in February the dormant spraying in the Central Valley in January was not captured. The air concentrations detected need to be compared with detailed pesticide use data around each monitoring site to evaluate how well air levels monitored represents exposure in neighborhoods closest to agricultural fields in the communities monitored and to provide data on times of year when different pesticides are used in each area. The draft report states that weather data were not collected on site in Ripon or Shafter and that the Department will use weather data from closest CIMIS station, 9.7 miles NW of Ripon site, 2.2 miles north of Shafter site. Wind data may not be representative at this distance.	The air monitoring network is designed to measure long-term ambient concentrations in communities from multiple pesticide applications and estimate subchronic and chronic exposures. DPR will compare total pesticide use within a region to the measured air concentrations, but detailed use data are not needed. DPR selected the three communities primarily because they are historically high use areas for multiple pesticides and the detected concentrations are similar to previous monitoring in Parlier. The pesticide use data will add context to the detected air concentrations, but DPR is confident in its conclusions. In contrast, detailed use data are essential in evaluating application-site monitoring data that DPR uses to estimate acute exposures. While 24-hour concentrations are given in the report, DPR will not use the air network data to estimate acute exposures. DPR will summarize the weather data to give context to the detected air concentrations, but DPR does intend to use computer modeling or other data analyses for which more accurate weather data might be needed. Moreover, if DPR were to conduct computer modeling, weather data at the application sites outside of the communities would be more valuable than weather within the communities.	*No changes to the report are needed*
17.	**Other suggestions –** At the PREC meeting, committee members were asked for recommendations regarding discontinuing monitoring of any of the target pesticides and whether the report should include cancer risk estimates. We have the following recommendations: a. unless DPR expects the use of acrolein as an aquatic herbicide near one of the three monitoring sites, discontinue reporting of acrolein data due to the previously mentioned concerns about analytical methods; b. include cancer risk estimates; and c. include in the report the proximity of expected use of the target pesticides to the monitoring sites (e.g., if one of the target pesticides is primarily used on a particular crop, indicate the approximate distance from each monitoring site to fields where that crop is grown).	DPR will proceed as follows with the following PREC recommendations: a. Acrolein reporting will be discontinued. b. Cancer risk estimates were included and appear on page 47 of the report. c. DPR will amend the report once pesticide use report data for 2011 are available	*Suggested changes to the report were made.*

Attachments: Comments Correspondence

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--Rural Housing Project
--Sustainable Communities Project
--Workers Rights Project

July 31, 2012

Edgar Vidrio
Environmental Monitoring Branch
California Department of Pesticide Regulation
(via email)

RE: Comments on Draft Report on Air Monitoring Network Results for 2011

Dear Dr. Vidrio:

We appreciate this opportunity to comment on the Draft Report on 2011 Air Monitoring Network results and offer the following observations and recommendations.

Comparison of Air Monitoring Results with Pesticide Use and Weather Data is vital.
This report explains that the Department will compare detected air concentrations with pesticide use patterns as well as weather conditions once the 2011 pesticide use reports have been compiled and verified. We think this step is vital and that for the most part it is premature to draw conclusions about the significance of air monitoring results before this further analysis is conducted. The conclusion in the summary that these air monitoring results indicate that buffer zones, application method restrictions and use limits appear to have been effective at reducing fumigant exposures below levels of concern is premature without an analysis of weather patterns and levels of fumigant use in proximity to each site. It is also premature to consider dropping any pesticides from further monitoring until after a comparison is made with pesticide use patterns and a full year of data is available. In addition, since 2011 sampling was initiated in February the dormant spraying in the Central Valley in January was not captured.

The air concentrations detected need to be compared with detailed pesticide use data around each monitoring site to evaluate how well air levels monitored represents exposure in neighborhoods closest to agricultural fields in the communities monitored and to provide data on times of year when different pesticides are used in each area. .

The draft report states that weather data were not collected on site in Ripon or Shafter and that the Department will use weather data from closest CIMIS station, 9.7 miles NW of Ripon site, 2.2 miles north of Shafter site. Wind data may not be representative at this distance.

Presentation of Data
In Table 4 results are reported in terms of percent of samples with detections of a given pesticide but it would have been more helpful if these were divided up by site. For example,. of the 40+ samples at a given site, how many had trace and quantifiable detections for each individual pesticide monitored.

Most or all of the pesticides listed on page 12 as EPA B2 carcinogens are also chemicals on the Proposition 65 list for cancer.

Disadvantages of sampling once a week revealed in monitoring results
In theory, sampling on a random day once a week should provide a representative sample. However, when the sampler malfunctions, as happened in Ripon several times, a significant amount of data is lost. In addition, the Department is now not sure they have an adequate number of data points to calculate cancer risk estimates. At the most recent PREC meeting, Randy Segawa said that the Department was considering doing a cancer risk estimate for 1,3 D but that with 5 detections it's hard to do the calculation or decide how to handle the samples with no detection.

To more accurately determine levels in the air when pesticides are used, a focused effort at peak times would give more information than picking 1 day randomly per week. When the PREC reviewed plans for the Air Monitoring Network, the ARB recommended sampling more frequently for specific pesticides during the times of year when those pesticides are used in an area. We urge the Department to reconsider this approach.

Salinas Site Concerns
During the site selection process the Air Resources Board expressed reservations about the Salinas airport site because it is located on the outskirts of Salinas, some distance from most crop land and while night time winds blow towards the airport from Salinas, day-time winds blow in from the bay diluting pesticide air levels. The residential areas of Salinas are also closer to crop land than the airport. The Department acknowledged that the airport was not their first choice for a Salinas site either.

We note that only trace levels of most of the non-fumigant pesticides sampled for were measured at the Salinas site during 2011 despite heavy use of many of these pesticides on crops grown in the Salinas valley. Air levels of methyl bromide were significant but substantially lower than levels measured by ARB at the Santa Maria site even though level of use of methyl bromide is similar in the two areas.

We urge the Department to consider relocating the Salinas site either to a more centrally located Salinas site or possibly south to Chular, Gonzales or Greenfield, communities previously identified as potential monitoring sites, to the Santa Maria site operated with ARB, or north to supplement sampling at the Watsonville school where some sampling is already being conducted in cooperation with the ARB. Due to the combination of past reservations about selection of this site and sampling results which seem out of synch with Salinas Valley pesticide use patterns we conclude it would be a waste of further time and resources to keep using this site until the 2011 pesticide use data can be analyzed.

Concerns about possible sampling and/or analytical limitations or problems
We are concerned that the Quantitation Limit for chloropicrin of 2,778 ng/m3 is higher than either the Sub-Chronic or Chronic Screening Levels and 12.5 times higher than the Detection Limit. It also seems strange that there were non unquantifiable detections of chloropicrin and only 3 quantifiable detections, all at the Salinas site.

We are concerned that the false positive results for DEF and now possibly methyl iodide raise questions about lab procedures but we have no expertise in this area. More blank samples between test samples may be advisable. We note that there was a large discrepancy in one pair of MITC duplicate samples. Average field spike percent recoveries were quite low for some pesticides and no ranges or standard deviations are reported. The response to the ARB audit discusses steps taken to address low recoveries with iprodione and MITC and chloropicrin only. The ARB audit on page 14 highlights some sampling problems including lack of an SOP for VOC sampling, storage of SUMMA canisters in refrigerator, incomplete chain of custody sheets, temperature of the storage refrigerator dropping below the accepted range, and tree possibly too close to sampling inlet at Ripon site.

Some Air Levels Measured Are of Health Concern

Methyl Bromide
DPR's seasonal) regulatory limit for methyl bromide of 19,400 ng/m3 (5 ppb) is not considered adequately health protective by OEHHA. OEHHA supports a seasonal or sub-chronic limit of 3,880 ng/m3 (1 ppb) to protect children. This was exceeded at the Salinas site as well as the Santa Maria and Oxnard sites.

Chloropicrin
The 1-day acute screening level for chloropicrin of 491,000 ng/m3 (73 ppb) is the regulatory level set by DPR management in the Chloropicrin Risk Management Directive. In contrast, the 24 hour acute screening level for children derived by DPR toxicologists in the TAC report is about 80 fold lower - 6,180 ng/m3 (0.92 ppb). The highest 24 hour concentration measured in Salinas, 3,926 ng/m3 was about 63% of the acute chloropicrin REL for children listed in the TAC report.

The seasonal chloropicrin screening level used is the same as the level derived in the TAC report. It is concerning that the Salinas site reached 78.9% of the chloropicrin sub-chronic screening level and 64% of the Acute Screening Level derived in the TAC report because this site is located further from major areas of fumigant use than the main residential areas of Salinas.

In the TAC report finalized by DPR in 2010, OEHHA, the SRP and DPR toxicologists all concluded that chloropicrin is a highly potent carcinogen so a calculation of cancer risk should also be included for chloropicrin utilizing the Cancer Potency HEC of $2.2(mg/kg/day)^{-1}$ and RfC for cancer of 0.24 ppt derived in the TAC report.

Chlorpyrifos and Diazinon
FQPA adjusted hazard quotients should be included in this report as they were in the Parlier report (at least in the draft I just looked at).

PANNA has derived a chlorpyrifos Subchronic Screening Level for children of 170 ng/m3, about 8 fold lower than the screening level of 850 ng/m3 used in this draft report.

Thank you for your consideration of these comments. Please contact me if you have any questions.

Sincerely,

Anne Katten, MPH
CRLAF Pesticide and Work Safety Project Director
(916) 446-7904 x 2019
akatten@crlaf.org

Reponses to Comments on the AIR MONITORING NETWORK RESULTS FOR 2011 - VOLUME 1

At the PREC meeting on July 20, 2012, you requested comments on the draft report "Air Monitoring Network Results for 2011." We have the following comments:

1. Sampling days – The third paragraph of the summary states that "24-hour samples were collected every week at each of the 3 sites." We suggest clarifying this sentence to indicate that one 24-hour sample was collected each week at each of the three sites.
2. Acrolein data – The fourth paragraph of the summary notes that "acrolein detections are consistent with statewide monitoring results from the Air Resources Board." Since the acrolein detections are attributed to automobile emissions and not to pesticidal use of acrolein, we recommend removing the sentence from the summary. In the body of the report when referring to acrolein data, if pesticide use data verifies that there were no pesticidal uses of acrolein near the three monitoring sites, we suggest inserting the following sentence: "(Note: ARB has reclassified their air monitoring results for acrolein as "unverified" due to concerns about analytical standards used to calibrate the analytical instruments.)"
3. Description of towns – The introduction describes the towns selected for monitoring. In those descriptions, the area of Shafter is listed as 28 square miles with a population of 16,988, while the area of Salinas is listed as 23.2 square miles with a population of 150,441. We suggest that you verify that the area of Shafter is actually larger than Salinas.
4. Laboratory audits – The data validation/quality assurance portion of the report describes audits of three laboratories: the CDFA Center for Analytical Chemistry, the ARB Organic Laboratory, and the ARB Inorganic Laboratory. The report summarizes the recommendations of the audits. We suggest clarifying if the recommendations apply to all three laboratories or just an individual laboratory.
5. Other suggestions – At the PREC meeting, committee members were asked for recommendations regarding discontinuing monitoring of any of the target pesticides and whether the report should include cancer risk estimates. We have the following recommendations:

    - unless DPR expects the use of acrolein as an aquatic herbicide near one of the three monitoring sites, discontinue reporting of acrolein data due to the previously mentioned concerns about analytical methods;
    - include cancer risk estimates; and
    - include in the report the proximity of expected use of the target pesticides to the monitoring sites (e.g., if one of the target pesticides is primarily used on a particular crop, indicate the approximate distance from each monitoring site to fields where that crop is grown).

Please contact me with any questions.

Lynton Baker
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August 31, 2012

VIA EMAIL (evidrio@cdpr.ca.gov)
Edgar Vidrio
Department of Pesticide Regulation
Environmental Monitoring
1001 I Street
Sacramento, CA 95814

Re: Draft Report with Air Monitoring Network Results for 2011

Dear Mr. Vidrio:

The Chloropicrin Manufacturers' Task Force (CMTF) appreciates the opportunity to provide comments on the draft report for the Air Monitoring Network Results for 2011. The CMTF represents registrants of products containing chloropicrin that are registered for use in California. The CMTF notes, as did DPR in its July 2012 press release, that the results from the air monitoring show that the pesticides monitored, including chloropicrin, are well below the health screening levels established by DPR. The CMTF offers the following comments on the draft report.

Risk Assessment Statements Outside of the Context of the Study Draft Report, Page 51

Page 51 contains the statement "*While the air concentrations are considered low, these pesticides had higher relative risk in comparison to the other AMN pesticides*." The pesticides referenced include the soil fumigants 1,3-dichloropropene, chloropicrin, methyl bromide and MITC. All of the air monitoring results for these pesticides were well below the DPR health screening guidelines for the specific pesticide. Moreover the Air Monitoring report is not a risk assessment for any specific pesticide, or an assessment of the comparative risk of monitored pesticides, but rather is an analysis of the potential presence of the listed pesticides in ambient air above selected screening levels. Therefore this statement and similar statements regarding risks are not within in the context of the study and should be removed from the report. These out-of-context statements serve no purpose and may confuse readers.

Incorrect 4-Week Average for Chloropicrin Draft Report, Page 20

The second sentence of the text on this page states that the maximum 4-week concentration of chloropicrin was 3,930 ng/m3. The correct value for the 4-week average is 1,810 ng/m3 as shown on table 7, page 21.

Explanation of Non- Detect Samples

In several places in the draft DPR does not adequately note and explain the impact of DPR's practice of (1) substituting a value of one-half of the Method Detection Limit (MDL) for samples with no detectable amount of the pesticide in question and (2) substituting the midpoint between the MDL and the Limit of Quantitation (LOQ) for trace samples. This practice produces an artificial screening level value that is treated as if it were an actual measured value. DPR's methodology is explained in the report; however the artificial nature of these values is not made clear each time the values are presented. Under the DPR methodology the mere fact of monitoring for a pesticide will create the artifact of the chemical being measured, even if it is not present. It is important that the reader understand that in some cases "% Screening Levels" are increased even where no measurable detections occurred. For example, no sample collected in Shafter and Ripon had detectable chloropicrin, yet the methodology results in an increase in screening levels for chloropicrin which were reported as 0.023% for acute exposure, 4.8% for 4-week exposure and 6.2% for chronic exposure. The CMTF urges DPR to stop using this approach for a monitoring study. At a minimum DPR should make clear that the values produced are not measured values and acknowledge the impacts of the approach on its percentage calculations.

Page 29, Appendix A Technical System Audit

The Technical System Audit indicates on Table 1 that the analytical method detection limit and the quantitation limit for chloropicrin were not developed at the time of the audit. The validation for these methods should be provided in the report.

The CMTF appreciates the opportunity to provide these comments on the draft report. Should you wish to discuss these comments further, we are available to meet with you at your convenience.

Sincerely

Stephen Wilhelm
Chairman
Chloropicrin Manufacturers' Task Force