

AIR MONITORING NETWORK UPDATE

DPR, Environmental Monitoring

Monitoring Plan

- Sampling started in February 2011
- Monitoring sites are located in:
 - Ripon, San Joaquin County
 - Salinas, Monterey County
 - Shafter, Kern County
- 1 set of 24-hour samples each week, each site
- Samples are analyzed for 34 pesticides

Number of Samples

- 628 samples collected and analyzed by February 1, 2012:
 - 154 multi-residue samples
 - 160 methyl isothiocyanate (MITC) samples
 - 158 chloropicrin samples
 - 156 volatile organic compound (VOC, fumigants) canister samples, 1 other sample invalid due to unacceptable ending pressure

Quality Control Samples

- 46 field duplicate samples
- 17 field “blank” samples
- 34 field “spike” samples (16 chemicals)
- 103 laboratory “blank” samples
- 96 laboratory “spike” samples

Preliminary Monitoring Results

- No concentrations over a health screening level, except acrolein (due to non-pesticidal sources)

VOC Issues

- Reporting Limit for VOCs (1,3-D, methyl bromide, methyl iodide) was lowered from 1.0 ppb to 0.1 ppb starting on 7/27/11
- Chronic screening level for methyl bromide is 1.0 ppb

Field and Lab Audit

- Some standard operating procedures (SOPs) and lab documentation were incomplete or had errors
- Sample storage was inconsistent with SOP
- VOC standard was out of date
- No VOC blind spikes

Quality Control Issues

- 2 positive field blanks
- 5 field spikes with no or trace detections
- Of 52 individual spiked concentrations, 20 out of control limits
- Field spikes issues
 - Incorrect solvent
 - May have spiked glass wool instead of sorbent
 - Narrow control limits

Unusual Detections at Salinas Site

Sample Date	S,S,S- tributylphosphorotrithioate (ng/m ³)
05/04/11	None detected
05/09/11	Trace*
05/18/11	None detected
05/23/11	Trace
06/01/11	None detected
06/06/11	Trace
06/16/11	None detected
06/20/11	Trace
06/29/11	None detected
07/05/11	Trace
07/11/11	None detected

*Reporting limit = 9 ng/m³, Screening level = 8,800 ng/m³

S,S,S-tributylphosphorotrithioate

- Tribufos, active ingredient in Folex (DEF no longer registered)
- Only registered as cotton defoliant
- Use is in fall in San Joaquin Valley and Imperial County

S,S,S-tributylphosphorotrithioate Followup

- Results appeared valid
 - LC/MS unequivocal method
 - Blanks had no detectable concentration
 - Samples are grouped and analyzed but detection in Salinas samples only
 - Field spike resulted in 85.5% recovery
- Unable to identify source near sampling site

S,S,S-tributylphosphorotrithioate Lab Review

- Further review indicated that most if not all detections were likely false positives
- Sequence of analysis caused “carryover” from spike into field samples
 1. 5 calibration standards
 2. Solvent flush
 3. Lab blank
 4. Lab spike
 5. Field samples (Salinas samples first in sequence)
- Detected in Feb 2012 Ripon sample, but not in duplicate
- Other pesticides may have carryover

Unresolved Quality Control Issues

- Control limits for spikes
 - Update limits based on more recent data?
- Carryover or other contamination
 - Other labs, instruments with similar issues?
 - Modify lab analysis?
 - Modify detection limit?
 - Drop from method?
 - Outside review, second lab?