Department of Pesticide Regulation
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STUDY #273: MODELING AND MONITORING FIELD EMISSIONS OF FUMIGANTS UNDER TOTALLY IMPERMEABLE FILMS (TIF)

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May 2011

I. INTRODUCTION

The Department of Pesticide Regulation (DPR) relies on the inventory of pesticide use for estimation of VOC emissions and achieving and maintaining federal ozone ambient air quality standards. The DPR historically assumed 100 percent of applied fumigants volatilize to the air and estimated the emissions accordingly. However, data collected from field monitoring studies indicated that fumigant emissions are less than 100 percent and vary with application method and managements practices. To establish the most accurate VOC emission estimation for fumigant application, a complete data set from fumigant emission studies describing chemical and physical properties of the fumigant and field properties should be requested for describing fumigant volatilization in the field.

A complete data set should consist of all physical and chemical properties of a fumigant product as well as all soil chemical and physical properties of soils where the field study was conducted. However, lack of availability of complete data sets describing properties of fumigants and conditions of field experiments created an important gap in understanding and evaluating processes of fumigant volatilization in the field. Recent attempts have been made for estimating cumulative emissions combining field and modeling efforts (Ha et al., 2009; Cryer and Wesenbeeck, 2009). However, lack of user-friendly multi-physics simulation models which require standardized input data creates great difficulties for state regulators with respect to validation and verification of the modeling and field results. Johnson (2008) indicated that such models can contain a biased and incorrect approach to estimate fumigant volatilization.

The Air Program (AP) of Environmental Monitoring Branch is looking more intensively into additional models to estimate fumigant VOC emissions. For modeling, the HYDRUS 1D and 2/3D multi-physics simulation software will be adapted for better estimating emission flux. The HYDRUS software will bring modeling standardization to flux estimation due to its potential enhancements and eventually provide a cost effective tool to describe/predict behavior of fumigants applied in an agricultural field. Successful prediction of fumigant fate and transport allows us investigate optimum management and application scenarios in reducing emissions into air. To perform modeling investigation, the AP needs a complete base case scenario (drip or shank injection of a bed or broadcast application) data set which would be used as an input to HDYRUS software. Thus, a field experiment will be conducted to measure all required chemical and physical properties of soil and other related parameters in fumigated field. After completion of the field experiment and modeling investigation with HYDRUS software, the AP will decide on requesting similar studies with data sets from registrants during their product registration process.

II. OBJECTIVE

The objective of this study is to establish a pilot field study for estimating emissions of two currently used fumigants into atmosphere and to compare the field data with HYDRUS and COMSOL modeling investigation.

III. PERSONNEL

The Environmental Monitoring Branch will conduct this study, under the overall supervision of Randy Segawa and Pam Wofford.
Other key personnel include:
Project Leader – Atac Tuli
Field Coordinator(s) – Jing Tao (Air sampling), and Fabio Sartori (Soil sampling)
Research or Senior Scientists – Bruce Johnson and Frank Spurlock
Statisticians – Bruce Johnson & Jing Tao
Other: USDA-ARS, Fresno - Suduan Gao; UC Davis, Salinas -Husein Ajwa

IV. SITE SELECTION

The study area will be chosen based on specific soil and logistic requirements located within Ventura County, an ozone non-attainment area where air quality improvements are needed. Although the location decision will be made upon meeting with all participating parties in the study, the general characteristics of the location are: 1) uniform soil depth around 80 cm with coarse to loam type soil texture, 2) field locations should be close enough to each other to minimize logistic problems during the study, but far enough apart to assure that field plumes do not interfere with each other. In addition, the study plots will be chosen to represent typical parameters followed by commercial agricultural production in Ventura County: 1) a seasonal application, 2) soil type and 3) application equipment. The location of the field will be verified with GPS systems with coordinates. Moreover, the coordinates of soil and air sampling locations will be measured with sensitive GPS units.

V. STUDY PLAN

This study plan relies on simplicity of the field study but focuses on intensive and broad measurement of chemical and physical properties. The broadcast shank injection method with one type of tarp cover will be used in all three field scenarios. The injection depth will be adapted as 18 inch in the application method and Totally Impermeable Film (TIF) will be used as tarp cover.

The study area will be located in Ventura County, California. The study will be conducted in three different fields with different tarp cutting times. The two out of three test fields will be 2-acre size and at least 4000 feet of separation from each other to prevent interferences. The third field will be 8 acres size. All fields will have a soil type that is typical of the area. The target soil moisture will be ~70% of field capacity.

Application Scenario #1 (Field 1): The combination of 1,3-dichloropropene and chloropicrin (Pic-Clor 60) fumigant mixture will be broadcast applied under a TIF tarp using at a rate of 600 lbs/acre at a depth between 16-21 inches for an average 18 inches. The shank application will be made with a Noble Plow, which consists of horizontal v-shaped blades mounted on the vertical arms of tool bars that inject fumigants laterally away from the shank. The Noble Plow has two 32 inch wide plows with a spacing that does not exceed 48 inches. In this scenario, TIF tarp will be cut when the concentration under tarp is less than 20 % of the initial concentration or on day 10 after fumigant application. For this application scenario, a 2-acre field will be used.

Application Scenario #2 (Field 2): The same fumigant product and rate will be used but in this scenario, TIF tarp cutting will be performed when the concentration under tarp is less than 10 % of the initial concentration or on day 14 after fumigant application. For this application scenario, a 2-acre field will be used.

Application Scenario #3 (Field 3): In this scenario, the same fumigant products and application rate will be used as in two previous application scenarios but TIF tarp cutting will be take place when the concentration under tarp is less than 5 % of the initial concentration or on day 18 after fumigant application. An 8-acre field will be used for this application scenario.

Air Sampling

The study design involves air monitoring around the treated field. The flux data will quantify the emissions rates of fumigants (μg $m^{-2}s^{-1}$) over time from the treated field. The off-site monitoring method will be used to back-calculate emissions from each field using sixteen and eight sampling stations for the one 8-acre and two 2-acre fields, respectively. In addition, the fields will be reasonably flat and free of obstacles around the edges, such as tree rows and houses. The land immediately surrounding the test fields will be reasonably flat land or agricultural fields that are fallow or have short crops (i.e., not exceeding 3 feet in height).

The off-site sampling equipment will be placed in 8 directions surrounding the 2-acre size fields: with two ‘rings’ consisting of four monitoring stations at approximately 26 feet from the sides of each field (4 stations), four monitoring stations at 32 feet from the corners of each field (4 stations) (Figure 1) . For the 8-acre field, the off-site sampling equipment will be placed in 16 directions around the field. Four stations will be located 98 feet from the corners and twelve monitoring stations will be at 32 feet from the side of the 8-acre field. The sample points will be approximately 5 feet (1.5 m) high to approximate the human breathing zone. Within 24 hours prior to application, background ambient air sampling will occur for approximately 12 hours at two off-site sample locations per field. The air sampling scheme is presented in Figure 1. The details of the air sampling schedule for application scenario #1 are given in Appendix A for designated two fumigants. The sampling schedules for the other application scenarios #2 and 3 will be determine based on the monitored fumigant concentration under the tarp. Air sampling schedule for scenario # 1 will be conducted as follows: The total period of air sampling during study is 14 days. Within 48 hours from start of the study or application, the air samples will be collected every 6 hours. At the end of 48 hours period, the sampling interval will be changed to 12 hours intervals until day 10 when the tarp cutting will be performed. After tarp cutting, the air sampling interval will be decreased to 6 hours interval for 24 hours period. At the end of 24 hours period (Day 10, 14 and 18), the 12 hours sampling interval will be resumed until study is ended based on application field and its scenario.

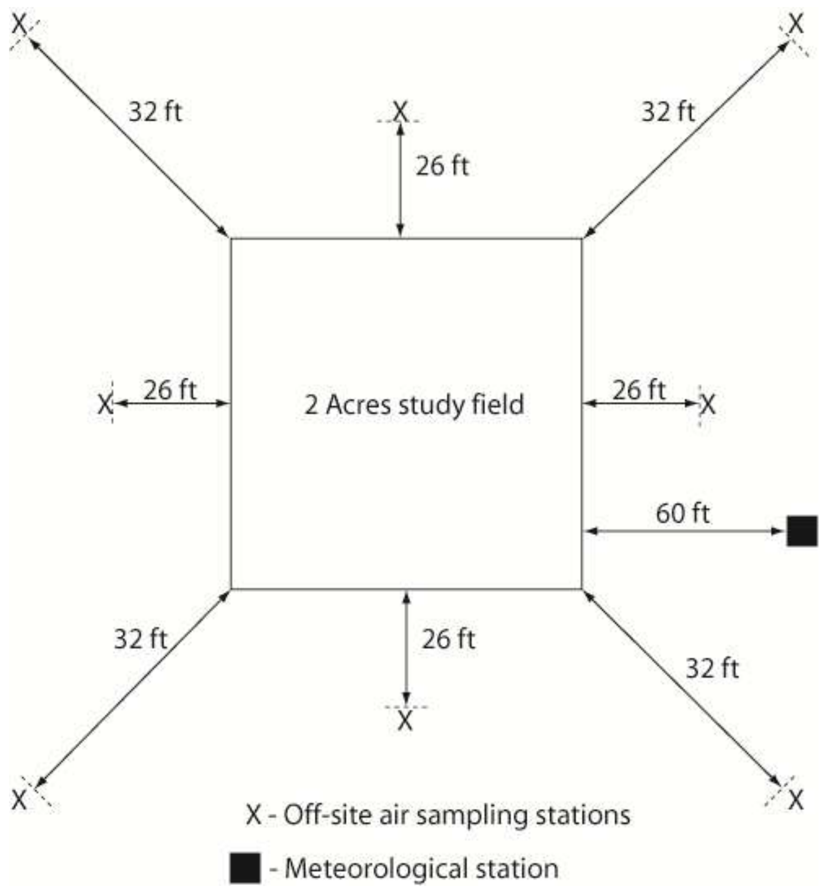

Figure 1. Off-site air sampling and meteorological station scheme.

For scenarios #2 and 3, the same air sampling pattern will be followed as scenario #1 until their respective tarp cutting day. After tarp cutting, the same air sampling schedule as scenario #1 will be followed for up to 7 days.
Air sampling tubes will be at 1.5 meter heights and attached air flow pumps will be calibrated to a flow of 100 to 1000 ml air per minute depending on the substance(s) to be monitored. The XAD and charcoal sampling tubes will be used for trapping chloropicrin and 1,3-dichloropropene, respectively.

Soil gas sampling
Soil gas sampling will be made by USDA-ARS, Fresno. Distribution of gaseous fumigants in soil profiles will be monitored using two repetitive composite probes in two

fields (8 acres and 2 acres) which will be provided by USDA-ARS, Fresno. Details of the sampling will be specified in a protocol written by USDA-ARS group.

Soil sampling for physical and chemical properties

Soil samples will be collected prior to application as given in Table 1. Undisturbed (Ring samplers) and disturbed soil samples will be collected at nine randomly selected locations at the 8-acre field (Table 1 and Figure 2). At each location, the soil samples will be collected from four depths (0-20 cm, 20-40 cm, 40-60 cm, 60-80 cm). From each defined depth, 1 ring (core) samples and 1-2 kg disturbed soil samples will be collected. The core samples will be covered on from both ends with plastic caps after properly trimming excess soil at the rings edges. The ring samples will be weighed at the field and the data will be recorded. This is necessary in order to determine initial water content during sampling. These samples need to be handled with extreme care since laboratory measurements of saturated hydraulic conductivity and soil water retention will be performed under assumption of field representing conditions. This kind of sample is also called an undisturbed sample. In addition, a disturbed loose soil sample will be taken using a shovel or auger from the corresponding depths of undisturbed soil samples. These samples will be stored in a plastic bag with a proper labeling. In addition to the 8-acre field, the two 2 acres fields will be sampled for undisturbed and disturbed conditions at 4 randomly selected locations. The estimated total amount of undisturbed samples will be 68.

Post application samples will be taken to determine status of the bulk density and water content. The sampling procedure will be similar to the pre-application sampling design (Table 2) and will follow Blake and Hartge (1986) or Garretson (1999). The estimated total number of undisturbed samples will be 68 as well. Our main goal in these sampling procedures is to obtain soil physical properties, which could best represent the pre- and post-application field soil conditions.

Soil analysis

After collection of core (undisturbed) samples, the samples will be weighed to determine initial moisture content and will be transferred to the laboratory for sequential determination of saturated hydraulic conductivity, soil water retention (0, 0.1, 0.3, and 1 bar pressure), and bulk density. In addition, the pre-application soil samples from each field will be analyzed for:

- Particle size (Texture)
- Cation exchange capacity
- Organic matter

The post-study samples will be taken after the flux monitoring is complete, and will be analyzed for soil moisture, saturated hydraulic conductivity, soil water retention (0, 0.1, 0.3, and 1 bar pressure), and bulk density.

Soil physical characterization will include determining the soil characteristic curves (soil water content at 0, 0.1, 0.3, 1 bar for undisturbed samples, and 3 and 15 bar for disturbed samples). Post-fumigation soil moisture will also be determined at the same depths listed above. Soil moisture will be determined by the gravimetric method by using soil cores for each 8 and 2-acre field, with segments of 0-20 cm, 20-40 cm, 40-60 cm, and 60-80 cm depths at each sampling location (Table 2).

Table 1. Soil sampling procedure before fumigant application

Scenario	Fumigant Product	Soil Sealing Method	Sampling location	Depths	Core Samples	Soil Samples
1	Telone/Pic mixture	TIF	4	0-20 cm	4	~2 kg
				20-40 cm	4	~2 kg
				40-60 cm	4	~2 kg
				60-80 cm	4	~2 kg
2	Telone/Pic mixture	TIF	4	0-20 cm	4	~2 kg
				20-40 cm	4	~2 kg
				40-60 cm	4	~2 kg
				60-80 cm	4	~2 kg
3	Telone/Pic mixture	TIF	9	0-20 cm	9	~2 kg
				20-40 cm	9	~2 kg
				40-60 cm	9	~2 kg
				60-80 cm	9	~2 kg
				Total Cores	**68**	

Table 2. Post application soil sampling procedure.

Scenario	Fumigant Product	Soil Sealing Method	Sampling location	Depths	Core Samples
1	Telone/Pic mixture	TIF	4	0-20 cm	4
				20-40 cm	4
				40-60 cm	4
				60-80 cm	4
2	Telone/Pic mixture	TIF	4	0-20 cm	4
				20-40 cm	4
				40-60 cm	4
				60-80 cm	4
3	Telone/Pic mixture	TIF	9	0-20 cm	9
				20-40 cm	9
				40-60 cm	9
				60-80 cm	9
				Total Cores	**68**

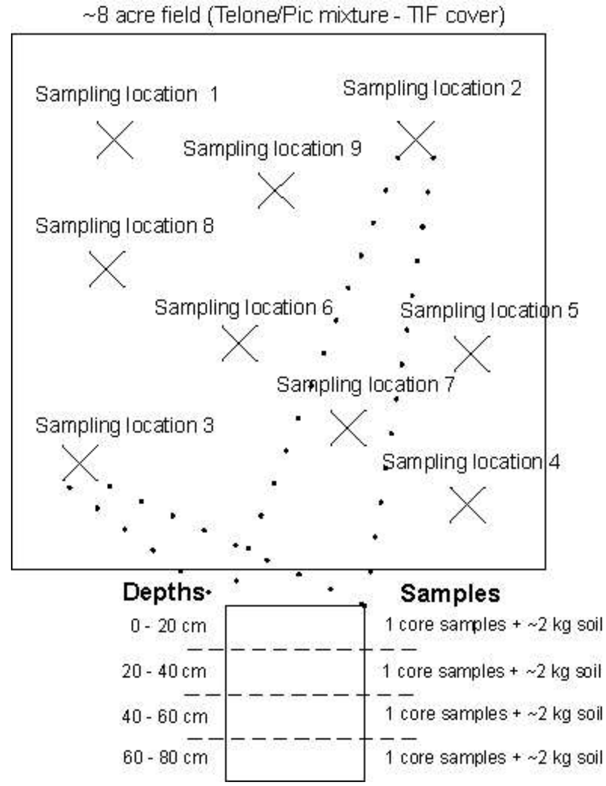

Figure 2. Schematic of soil sampling procedure of pre-application conditions.

Bulk density will be derived from the dry weight of the soil and the known volume of soil cores (Blake and Hartge, 1986). Soil texture will be determined by the Bouyoucos Hydrometer Method or similar validated method (Gee and Bauder, 1986). The general presence of clods, stones and crop residue will be recorded. The total organic carbon will be determined by dry combustion method (Nelson and Sommers, 1996). Analyses of soil texture, organic matter, bulk density, and soil water content will be performed in our laboratory facility at DPR's West Sacramento Warehouse.

In-situ soil temperature, moisture and electrical conductivity monitoring

The soil temperature, moisture dynamic and electrical conductivity during period of study along soil depths under tarp conditions will be monitored simultaneously at two locations nearby the study fields where the application equipment will make an extra pass and lay tarp but will not inject fumigants (Table 3). The measurements will be performed with 5TE sensors that purchased from Decagon Devices, INC. At the each location in the extra pass, the total of four 5TEs will be installed at the center of the extra pass at depth segments of 0-20 cm, 20-40 cm, 40-60 cm, and 60-80 cm corresponding one 5TE for each depth segment (Figure 3). Every installed 5TEs will be connected to EM50R data logger with 10-minute reading intervals. The collected data will be transferred via Data Collection base station to the computer. Moreover, two pressure transducers and thermocouples and three relative humidity sensors will installed between soil surface and TIF tarp in the extra pass for monitoring changes in pressure, temperature and relative humidity, respectively. The relative humidity sensor will have additional temperature measurement for ensuring accuracy of the air temperature measurements by thermocouples.

Table 3. *Soil and soil surface instrumentation under tarp*

Instruments	**Measured parameter**
5TE	Soil Moisture, Temperature, Electrical Conductivity
Pressure transducers	Pressure underneath TARP
Thermocouples	Temperature at the soil surface under trap
12-bit Temperature/RH smart sensor	Temperature and Relative Humidity under tarp

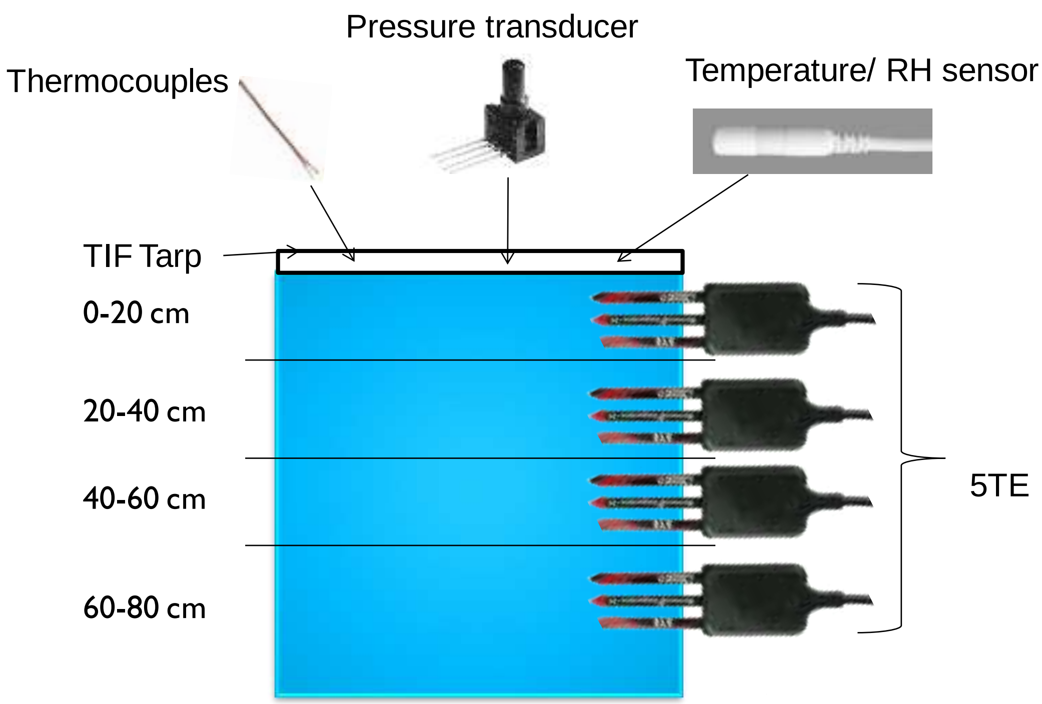

Figure 3. Schematic of installation of soil sensors and instruments.

Tarp thickness and permeability measurements

The tarp thickness and permeability measurements will be made by Husein Ajwa at UC Davis. Ten representative tarp samples (each sample will be 1 m^2) will be collected from each field after tarp splitting. In addition ten unused samples will be collected from each roll. The thickness of the tarp will be measured on all samples. Three samples from each field will be randomly selected and will be used to measure tarp permeability (Mass Transfer Coefficient) to chloropicrin and 1,3-dichloropropene using static permeability cells (Papiernik et al., 2001; Yates et al., 2008). The before and after tarp permeability measurements will be made using three different temperatures (10, 25, and 40 ^oC).

Field and meteorological data collection
A meteorological system will be installed at each field (Figure 1). The instrumentation and meteorological parameters will be decided by Environmental monitoring personnel of DPR. Cloud cover data will be obtained from a State- or privately-operated meteorological station in nearby location of study area, as well as onsite estimates of percent cloud cover being recorded on the air sampling sheets. Additional data, such as barometric pressure, will be collected and compared with the nearest state or U.S. National Oceanic and Atmospheric Administration (NOAA) weather station. In addition, pressure changes of the air pocket between tarp and soil surface will be monitored by pressure transducers. Summary of the meteorological parameters which will be measured during field study, are presented in Table 3.

Analysis of off-site concentration data for determining flux
Each monitoring period will be analyzed to estimate flux. The analysis will follow guidelines presented in Johnson et al. (1999). In short, hourly meteorological data will be assembled for each monitoring period. Monitored concentrations and field geometry together with meteorological data will be input into ISCST3. A nominal flux rate will be used to run ISCST3 and the nominal flux rate will be adjusted to achieve best agreement with the measured values based on a regression of measured versus modeled values. This adjusted flux will be used as the estimated flux for the time period.

Table 3: Meteorological Parameters Measured During the Field Study

Parameter	Monitoring Height (ft)	Averaging Periods
Wind speed	6 and 30	1 minute, hourly
Wind direction	6 and 30	1 minute, hourly
Stnd. dev. Horizontal wind direction	6 and 30	1 minute, hourly
Stnd. dev. Vertical wind speed	(do we need this?)	1 minute, hourly
Ambient air temperature	1, 3, 6, 10, 20	15 minutes
Relative humidity	10	15 minutes
Solar radiation	10	15 minutes
Precipitation	10	15 minutes
Atmospheric pressure	0-0.06 and 5	15 minutes

Transport modeling for estimating post-application fumigant volatilization
After data analysis, the processed data from field study will be used as an input to HYDRUS 2/3D and COMSOL simulation models for estimating post-application fumigant volatilization. The model results will be compared with the measured soil gas concentration and fumigant fluxes. This will allow us to evaluate model performances and to understand processes in estimating fumigant volatilization. Moreover, using inverse technique and simulations models (HYDRUS and COMSOL), unknown parameters (e.g. degradation coefficient) describing fumigants fate in the soil will be estimated.

VI. TIMETABLE

Field study and soil sampling: May-June 2011
Handling soil samples for physical properties: July-September 2011
Data analysis and modeling: October 2011-February 2012
Report Preparation: March 2012-June 2012

VII. REFERENCES

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Appendix A: Air sampling schedule for scenario #1.

Sampling Period	Date*	Estimated Time	Hours after Start of Application	Comments
Period 0	5/24/2011	1900	-12	Background samples plus Fortified and Blank samples
Period 1	5/25/2011	0700	0	Start applications
Period 2	5/25/2011	1300	6	
Period 3	5/25/2011	1900	12	
Period 4	5/26/2011	0100	18	
Period 5	5/26/2011	0700	24	
Period 6	5/26/2011	1300	30	
Period 7	5/26/2011	1900	36	
Period 8	5/27/2011	0100	42	
Period 9	5/27/2011	0700	48	
Period 10	5/27/2011	1900	60	Blank samples
Period 11	5/28/2011	0700	72	
Period 12	5/28/2011	1900	84	
Period 13	5/29/2011	0700	96	
Period 14	5/29/2011	1900	108	
Period 15	5/30/2011	0700	120	
Period 16	5/30/2011	1900	132	Blank samples
Period 17	5/31/2011	0700	144	
Period 18	5/31/2011	1900	150	
Period 19	6/01/2011	0700	156	
Period 20	6/01/2011	1900	162	
Period 21	6/02/2011	0700	168	
Period 22	6/02/2011	1900	180	
Period 23	6/03/2011	0700	192	Tarp Splitting
Period 24	6/03/2011	1300	204	
Period 25	6/03/2011	1900	216	
Period 26	6/04/2011	0100	228	
Period 27	6/04/2011	0700	240	
Period 28	6/04/2011	1900	252	
Period 29	6/05/2011	0700	264	Tarp Removal
Period 30	6/05/2011	1900	276	
Period 31	6/06/2011	0700	288	
Period 32	6/06/2011	1900	300	
Period 33	6/07/2011	0700	312	
Period 34	6/07/2011	1900	324	Fortified and Blank Samples

* This is a tentative starting date and schedule.

Appendix B: Soil air sampling schedule for scenario #1.

Sampling Period	Date*	Estimated Time	Hours after Start of Application	Comments
Period 1	5/25/2011	1300	6	After start of applications
Period 2	5/25/2011	1900	12	
Period 3	5/26/2011	0700	24	
Period 4	5/27/2011	0700	48	
Period 5	5/28/2011	0700	72	
Period 6	5/30/2011	0700	120	
Period 7	6/01/2011	0700	168	
Period 8	6/03/2011	1300	222	Tarp splitting
Period 9	6/05/2011	0700	262	Tarp removal
Period 10	6/08/2011	0700	334	
Period 11	6/08/2011	1900	346	Fortified and Blank Samples

* This is a tentative starting date and schedule.