Department of Pesticide Regulation

Mary-Ann Warmerdam
Director

Arnold Schwarzenegger
Governor

M E M O R A N D U M

TO: Randy Segawa
Environmental Program Manager I
Environmental Monitoring Branch

FROM: Bruce Johnson, Ph.D. *Original signed by*
Research Scientist III
Environmental Monitoring Branch
916-324-4106

Frank C. Spurlock, Ph.D. *Original signed by*
Research Scientist III
Environmental Monitoring Branch

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SUBJECT: A METHOD FOR ESTIMATING NEAR-FIELD AIR CONCENTRATIONS FOLLOWING TARP CUTTING FOR BROADCAST APPLICATIONS

Background

Fumigant applications in California comprised about 20% of the 163 million pounds of the top 100 pesticides applied in California in 2010 (DPR 2010). Tarps are often used to cover the field following fumigation. Tarps vary in permeability, and the new totally impermeable films (TIF) appear to have especially low permeability; they are expected to hold fumigants in the soil longer. This is desirable because there is the potential to reduce buffer zones and reduce application rates while maintaining efficacy because soil concentrations remain higher longer. However, when such tarps are cut, there is greater possibility for volatilization than with tarps that are more permeable. An important question is how long should the tarp holding period last in order to reduce the potential need for buffer zones at the time of tarp-cutting.

The Department of Pesticide Regulation (DPR) planned a field experiment to obtain data to test holding periods. The study was conducted in June 2011. It involved a broadcast application of Pic-Clor 60, consisting of 39% 1,3-dichloroprene (1,3-d) and 59.4% chloropicrin (Ajwa et al. 2011). The fumigant was shanked in to a depth of 18 inches and the entire application area covered with a TIF. The original question posed to us was if it would be possible to determine, based on daily soil-tarp gap air concentrations, when tarp-cutting could be safely done in order to avoid exceeding health reference levels at the edge of field, thereby avoiding any buffer zone requirement for either 1,3-d or chloropicrin. The air concentration reference level for 1,3-d is 160 ug/m3 (24 hour average) and for chloropicrin is 203 ug/m3 (50 ppb, 1-hour average).

In the course of planning for the field study, a second issue arose: the possibility that monitoring during the post-tarp cutting period would produce no measureable concentrations. This situation arose with flux profile studies utilizing small one acre fields and relatively impermeable tarps where chloropicrin had been applied (Ajwa 2010). In some cases entire monitoring periods consisted of nondetects. Having a high percentage of nondetects from the off-site monitors creates significant difficulties for calculating flux and generalizing results to other situations, such as larger treated acreages and/or higher application rates (Barry and Tao 2011).

During the tarped interval, the active ingredients undergo loss from the soil due to degradation and volatilization, two processes with inherent variability. Degradation half-lives are highly variable (Dungan et al., 2003) and depend on soil properties which themselves are variable.

Tarp performance in laboratory tests may be different than tarp performance in the field. Reasons include potential tarp defects associated with application (tearing, stretching or punctures) and humidity effects on tarp permeability. A "TIF" was used in a drip irrigation field study with methyl bromide and chloropicrin (Ajwa et al. 2009). The study found losses of 26% of the applied chloropicrin. Therefore, it cannot be assumed that the film is literally totally impermeable. On the other hand, laboratory measurements on TIF tarps do indicate generally low permeability. Thus, actual TIF permeabilities in the field are uncertain. The uncertainties in both degradation and tarp permeability present a problem for field studies intended to evaluate appropriate post-application tarping periods. If tarp permeabilities are in fact very low, tarp-cutting in such studies may occur but result in a large flush of fumigant from under the tarp into the air, thereby exceeding health protective reference air concentrations close to, but not in the field. Consequently, it is desirable to have a method for predicting the immediate post-tarp cut fumigant flux using in-field surrogate measurements such as under tarp air concentrations.

An added consideration is the necessity not only to answer this question for the contemplated field study, which has a specific acreage and specific application rate, but to devise a general method to answer the question for other acreages or application rates.

The objectives of this memorandum are:

(1) to devise a general procedure to answer the question: "Based on daily tarp-soil air concentration measurements, how long should 1,3-d and chloropicrin be retained before tarp cutting so that volatilization after tarp cutting will not result in exceedances of reference concentrations at the edge of the field?"
(2) to analyze relevant factors to assure ourselves that post tarp-cutting air concentrations in the Lost Hills study will be above the detection limit. It is important to obtain measurable concentrations in order to scale results up to bigger acreages or higher application rates.

The development of answers to these questions is complex and we have broken it down into three phases.

Phase 1: Use of the Hydrus2D/3D modeling package to estimate (1) tarp-soil air gap concentrations during the tarping period and (2) volatilization after tarp cutting over a variety of scenarios.

Phase 2: Analysis of the results from Phase 1 to determine relationships between (1) soil-tarp air gap fumigant concentrations, (2) total residual fumigant mass in shallow soil layers that may contribute to volatilization shortly after tarp-cutting, and (3) 6 hour and 24 hour volatilization flux following tarp cutting.

Phase 3: Use of ISCST3 to develop a basis for estimating air concentrations in the vicinity of field. Together with the Hydrus simulation results, we will calculate probabilities for exceeding the reference concentrations during the six hour period following tarp cutting. In addition, we will calculate probabilities for nondetectable samples arising during that same six hour period. We will suggest ways in which the results of this analysis could be generalized to other situations.

Modifications have recently been made to Hydrus 1D and Hydrus 2D/3D software to improve their ability to simulate fumigant transport and volatilization under realistic field conditions (DPR contract 09-C-0078). The modifications were made by the program author, Dr. J. Šimůnek at UC Riverside (Šimůnek undated), and DPR has tested the modifications to ensure their computational integrity (Spurlock 2009, Spurlock 2010, Spurlock et al. 2010). During the period that the analysis in this memorandum was being developed, the field study was conducted in June, 2011 near Lost Hills, California. The field study utilized two 2-acre fields and one 8-acre field which were broadcast tarped after being fumigated with 1,3-d and chloropicrin. The tarps were cut after 5 d, 10 d, and 16 d. We have completed development of this predictive method and finalized the predictive results in this memorandum without knowledge of the study results to avoid any bias.

Phase 1. Use of modified Hydrus 2D/3D modeling package to estimate (1) soil mass residuals during tarping phase and (2) volatilization after tarp cutting

Background: There are several considerations in setting up simulation scenarios to provide useful estimates of fumigant soil mass residuals and volatilization. These include the size of the "gap" between the soil surface and the tarp, the permeability of the tarp, soil type and appropriate associated soil physical parameters, initial soil moisture content, and physicochemical parameters for the active ingredients. Phase 1 required several scenarios designed to bracket a range of conditions. We discuss each of these elements.

Soil-tarp gap: The agricultural soil surface is not perfectly flat. The definition of soil surface itself is somewhat ambiguous because of its fractal nature. A tarp does not contact the entire soil surface, but some fraction of the surface. Figure 1 depicts a bedded tarp where a dirt clod visible in the right center of the picture elevates the tarp above surrounding soil surfaces. This results in an air gap between the soil and the tarp. There are obvious tarp-stretch lines emanating from the point of contact. A fumigant will diffuse out of the soil into this air gap before diffusing through the tarp into the atmosphere. The initial flux following tarp cutting will include a contribution from the immediate release of fumigant from the soil-tarp air gap.

Intuitively, the volume of the air gap will depend upon the roughness of the soil. Larger clods will lead to a larger volume. In order to get some framework for assessing this volume, we looked at soil roughness studies. Several studies have measured variation in soil height at a relatively small scale of 0.5-1.0 cm

For the most part, these studies were aimed at examining the relationship between spectral scatter and surface roughness in order to remotely assess roughness from aerial or satellite imagery. The typical method involves taking soil height measurements along a transect from 1.0 to several meters long at 0.5 to 1.0 cm intervals. Such measurements have been taken using a pin board or with laser devices mounted on tracks. Typically a regression is fit to each transect. The regression is used to arithmetically level the measurements. Then the root mean square deviation (RMS) is calculated. This is the measure of surface roughness.

Davidson et al. (undated) classified a range of soil smoothness from ploughed to rolled (Table 1). The rolled surface was "smoother" with clods more broken down. The roughest surface exhibited RMSs of 2 to 5 cm compared to the least rough surface at 0.5 to 1.5 cm. Similarly Matthias et al. (2000) looked at a fine sandy loam and clay loam soil. The "rough plowed" category was 3.0 to 3.75 cm RMS. This compared to their smoothest soil, called "seedbed," which was 1.6 to 1.8 cm RMS. Thus for agricultural soils, a range of 1 to 4 cm seems reasonable for the RMS of the soil height.

Permeability of the tarp: Permeability is measured by the mass transfer coefficient (MTC) with units of velocity (distance/time). Recent tarp permeability measurements have largely followed the techniques pioneered by Papiernik et al. (2001, 2010), which have been adopted by the U.S. Environmental Protection Agency (EPA) (Qian et al, undated). This technique involves use of two small metal chambers which are separated by a tarp sample. The fumigant is introduced into one chamber and measurements of air concentration on both sides of chamber are taken over time. These concentrations decline in the source chamber and increase in the receiving chamber. The concentrations are fit to a mathematical model to estimate the mass transfer coefficient. When this current work was started, there were few reports providing TIF tarp permeability measurements. Ajwa (2008) found 0.001 cm/h to 0.09 cm/h for 1,3-d or chloropicrin in fresh "virtually impermeable film" (VIF) or TIF tarps ('Before' columns in Table 2). The other tarp types exhibited larger MTCs. Weathering of the tarp ("After" columns in Table 2) increased MTC as much as an order of magnitude in the VIF and TIF tarps. Ajwa (2008) does not quantify the amount of time the tarp was in the field: "The permeability of several fumigants (1,3-d, chloropicrin, iodomethane, and methyl bromide) were determined before and after tarping."

As a comparison to Ajwa's measurements, Papiernik et al. (2010) measured permeabilities for many tarps and fumigants. VIF tarps are comparable in permeability to TIF tarps. Papiernik et al. (2010) summarize VIF tarp permeabilities over several different manufacturers for cis- and trans-1,3-d and chloropicrin (Table 3). Minimum and maximum values span two orders of magnitude (Table 3). The median MTCs for 1,3-d isomers were 0.00361-0.008 cm/h and 0.00008 cm/h for chloropicrin. The large standard deviations reflect high variability.

Since this work was started, the U.S. EPA has also tested many tarps, including the TIF type. Their methods are written up (Qian et al., undated), but as far as we can tell, the data is not published. We obtained it from Qian (Qian personal communication) via e-mail. Under ambient humidity, the median MTCs for 1,3-d isomers and chloropicrin were similar at about 0.0002-0.0003 cm/h (Table 4). In some cases, tarps exhibited no measurable permeability over several hundred hours of testing (minimum MTC of 0, Table 4).

The U.S. EPA also tested the impact of humidity and found high humidity generally increased permeability. The median increased by 2 orders of magnitude for 1,3-d and 1 order of magnitude for chloropicrin (Table 5), compared to the values at ambient humidity (Table 4). The humidity effect creates uncertainty in translating from laboratory to field MTCs. Below-tarp humidities under field conditions may be high as evidenced by condensation on the underside of the tarp (Figure 1).

The laboratory-measured MTCs must be appraised with some appreciation for the effects of field applications on tarp integrity and the volatilization process. Ajwa (2008) measured tarp permeabilities to several fumigants (1,3-d, chloropicrin, iodomethane, and methyl bromide) before and after field tarping. Ajwa reported that weathering of the tarp in the field increased MTC as much as an order of magnitude in the VIF and TIF tarps ("After" columns in Table 2). Ajwa (2008) does not quantify the amount of time the tarp was in the field. In a second study, Ajwa et al. (2009) found methyl bromide and chloropicrin losses of 45% and 26%, respectively, in a drip application with a TIF covering. The authors evidently expected much lower losses, perhaps more consistent with the low MTCs reported from the laboratory film studies. In explaining their results, the authors state:

> "While the TIF demonstrated significant emissions reduction for both methyl bromide and chloropicrin compared to LDPE (*low density polyethylene*), the peak and total emissions for both compounds under both film types were uncharacteristically high. High early MB and Pic emission rates and mass losses from the TIF field were believed to be due to significant leaks in the drip irrigation

> systems during the application. A significant volume of irrigation water was discovered at one corner of the fields immediately after application. This leak in the irrigation line is likely the leading contributor to the high early volatilization losses found in this study. Lack of emulsifier in the formulation (1.6% instead of 5%) may have also contributed to the volatilization losses of fumigants from the dry, uncovered furrows in both fields. In addition, the field preparation in Field 1 was substandard in that large clods were present at the soil surface. Cloddy surface conditions are conducive to allowing the escape of fumigant emissions. In some areas of the field, these clods also created many small punctures in the film, thereby compromising the film's integrity" (pages 51-3, Ajwa et al. 2009).

Thus, in implementing and assessing a computer simulation based on laboratory measured MTCs, the actual field MTC will probably be higher than the laboratory measured MTC. In Ajwa et al. (2009) the unexpectedly higher emissions were partly explained by leakage, which is independent of MTCs and by tarp defects that occurred during application such as stretching, tearing or puncturing. Thus the "field MTC" may be different from laboratory tests, which always utilize intact film samples for testing.

A list of possible reasons for apparent increased "field MTC" compared to laboratory-measured MTC are (1) tarp tearing during application, (2) defective gluing operations, (3) tarp punctures from animals, (4) thin spots due to stretching, (5) tarp weathering, (6) gas escape from the edges, and (7) high sub-tarp humidity. Figure 2 depicts a bedded tarp application for 1,3-d and chloropicrin (DPR photo archive). The beds and tarp application are uniform and geometric. In a small blown-up section from Figure 2 possible punctures are visible in the tarp (Figure 3). These field factors will affect "field MTC" to an unknown degree.

For purposes of simulation, two conditions were represented: a higher and lower permeable tarp. At the time that the simulations were being prepared, there was almost no TIF data. VIF data was used as a proxy for TIF. Given the wide range of MTCs for 1,3-d and chloropicrin, a high and low MTC of 0.0005 cm/h and 0.14 cm/h were chosen. HYDRUS uses an equivalent boundary layer at the soil surface to simulate the volatilization resistance of a tarp. The chosen MTCs corresponded to boundary layer thicknesses d of 57400 cm and 2000 cm, respectively. The thickness d is calculated as $d=D_g/\text{MTC}$, where D_g=287 cm^2/h, the approximate gaseous diffusion constant for chloropicrin. Preliminary Hydrus simulations estimated very low flux for both boundary conditions (<3% over 7-d). Therefore, we increased the permeability of the low barrier scenario by changing d from 2000cm to 500cm in order to provide greater contrast (9% volatilization after 7d). The 500 cm condition corresponds to an MTC of 0.57, which is the same order of magnitude as the maximum TIF measured permeabilities under conditions of high humidity (Table 5). The use of this higher MTC is justified because field-estimated fluxes exceeding 25% of the applied material were found for methyl bromide and chloropicrin despite use of a TIF (Ajwa et al. 2009).

Soil type: Sandy loam soils are the most common soil for application of soil fumigants (Johnson and Spurlock, 2008). The van Genuchten soil hydraulic model (van Genuchten 1980) was used to describe the relationship between soil water matric potential (*h, cm*) and water content (θ). As applied here, that model uses four parameters: residual water content (θ_r), saturated water content (θ_s), and two empirical variables α (cm^{-1}) and N. These parameters are collectively referred to here as "VG parameters". Spurlock (2008) calculated four average VG parameters for 27 sandy loam soils, where those soils were selected based on availability of a wide range of $\theta(h)$ data in the UNSODA database (Leij et al. 1996). Subsequently, the medians of the four parameters have been found to better describe the aggregate $\theta(h)$ data for the 27 soils as compared to average parameters (Spurlock, personal communication). The median VG parameters for Sandy Loam used here were $\theta_r = 0.01130$, $\theta_s = 0.39920$, $\alpha = 0.01660$ and $N = 1.30430$. The air-gap between the soil surface and the tarp was simulated as a high-porosity porous medium. The VG parameters for this region were $\theta_r = 0.00$ (zero), $\theta_s = 0.95$, $\alpha = 0.075$ and $N = 1.89$. This parameter combination for the air-gap yielded high porosity and very low water content over the range of matric potential observed in the simulations.

Initial soil moisture content: Soil fumigant product labels generally require a certain range of soil water content at the time of application. For example, recently imposed "Good Agricultural Practices" (GAP) for methyl bromide, chloropicrin and MITC-generating fumigants mandate soil water contents in the range of 50% - 75% of available soil water. Available at: (<http://www.epa.gov/oppsrrd1/reregistration/soil_fumigants/implementing-new-safety-measures.html>). Available soil water is that water held in the soil between field capacity and the permanent wilting point. Using the median VG parameters above, we calculated field capacity of our model Sandy Loam soil as 0.237 (h = -330 cm) and the permanent wilting point as 0.084 (h = -15000 cm). Using these data, an initial soil water matric potential of - 1000 cm was chosen, corresponding to an initial water content throughout the profile of 0.175 that fell within the GAP range.

Soil surface temperature: Diurnal soil surface temperature variations were simulated using the HYDRUS 2D/3D – supplied sine wave temperature option. That option describes soil surface temperature as a sine function with user-specified average temperature and amplitude. The average soil temperature selected here was 20C and the specified amplitude was 15C. The maximum temperature occurs at 1300 hours each day and is hard-coded into the program. HYDRUS 2D/3D-supplied default soil thermal conductivity and heat capacity data for sands were used to simulate heat transport.

Chemical properties: The chemical properties for 1,3-d and chloropicrin (Table 6) were obtained from various literature sources as cited in the review by Spurlock (2010). The soil-water distribution coefficient was estimated from the organic-carbon normalized soil-water distribution

K_{OC} assuming an average soil organic carbon content throughout the entire 150 cm profile of 0.001. A bulk density of 1.50 g cm^3 was assumed.

Scenarios: Four scenarios were utilized to span a range of tarp holding times before tarp cutting and a range of air gap fumigant masses below the tarp. Tarp holding times of 7 and 21 days were used. Two values for the air-gap thickness were used, 1 cm and 4 cm. Different tarp MTCs were used with the two air gaps, with 57000 cm assigned to the 4 cm case and 500 cm assigned to the 1 cm case. In theory one might want to cross the MTC with the other two factors, yielding eight cases. We were interested in extremes and reasoned that a large air gap volume combined with a low permeability would constitute one extreme and a more permeable tarp with small air gap would constitute the other extreme. Each fumigant was run separately leading to a total of eight scenarios (Table 7).

Running the Hydrus 2D/3D model was accomplished with two serial simulations for each of the eight cases. The first stage for each case consisted of the period from application to tarp-cut. The second stage consisted of a 3.5 day post-tarp-cut period. In the first stage, the 150cm x 150 cm soil domain was seeded with an initial concentration of 1 ug/cm3 in a 10 cm horizontal band at 36 to 46 cm below the surface (commonly, a shank application for 1,3-d uses an 18" depth, or about 45 cm). This application mass was 11.593 ug/cm^2 (=1739 ug/150 cm^2), which corresponds to 1.034 lbs/ac (=11.593 ug/cm^2 *x* (1 lb/acre)/(11.21 ug/cm^2). Fumigant soil concentrations and fluxes are linearly related to application rate. Thus numerical results from the simulations can utilize this modeling application rate to scale up results to field application rates. The soil conditions at the end of the stage 1 simulations (temperature, water content and fumigant concentration) were used as initial conditions for the stage 2 simulations in order to complete the scenarios.

Typically, at the end of the initial holding period, broadcast tarps are perforated ("cut") by driving a small all-terrain vehicle equipped with a trailing knife rapidly over the tarped surface, slicing the tarp in the process. As a result, a relatively narrow region of the tarped soil is then "open" to the atmosphere (Figure 4). The new dual volatilization boundary condition (BC) of the modified Hydrus package was used to simulate this surface condition in the second modeling stage. This BC allowed the equivalent boundary layer of the intact tarp to be simulated (d = 57000 or 500 cm, depending on the scenario) along with a much smaller equivalent boundary layer depth of 0.5 cm at the tarp-cut location. Jury et al. (1986) recommend d = 0.5 cm as a representative value for bare soil.

Simulation output elements: The soil profile was divided into seven subregions (layers) and observation nodes for each subregion were assigned (Table 8). We attempted to establish similar soil profiles for these two scenarios. The differing size of the air gap in subregion 1 caused minor differences in defining the soil subregions. The Stage 1 soil subregions in Table 8 were maintained in Stage 2 of the simulation procedure. The observation nodes were located in the middle of each subregion. Key output included soil mass distribution by subregion over time, concentrations at the observation nodes, cumulative flux into the atmosphere, and mass balance as a check on numerical integrity. Targeted observations included the concentration in the soil-tarp air gap, concentration in the soil layer just below the soil-tarp air gap, total mass in the top 5 cm, which was a weighted average of the mass in the soil-tarp air gap and the soil layer just below it to achieve a depth of 5 cm. For the 4 cm soil-tarp air gap, the mass represents the total mass in the soil air gap plus 1/11 of the mass in the soil layer immediately below since that soil layer was 11 cm thick. For the 1 cm soil-tarp air gap, the mass in the top 5 cm represents the sum of the mass in the 1 cm soil air gap plus 4/10 of the mass in the adjacent soil layer, which was 10 cm thick.

Results Phase 1

Mass balances during the Hydrus simulated tarp holding periods were good with the maximum error at 1.03% occurring in the chloropicrin high permeable 21 day simulation (Table 9). Generally, the results reflected the obvious differences in simulation conditions during the holding periods. The more permeable tarp scenarios showed less remaining fumigant mass in the soil at the end of holding period than the less permeable tarp scenarios. Corollary to that, the total mass volatilized during the holding period was higher for the more permeable tarp scenarios, C3 and C5. Similarly, longer holding times showed lower mass left in the soil, due to the combined losses from volatilization and degradation. Chloropicrin, with a 3.5d half-life, was more quickly degraded compared to 1,3-d with the 7d half-life. For example, the high barrier tarp (57400 cm) 21 day hold (case 1C4) resulted in 215.9 ug/cm of 1,3-d left in the soil compared to 27.46 ug/cm for chloropicrin (Table 9).

Post tarp cut volatilization reflected the scenarios in a consistent and straightforward manner. Short holding time produced greater flux and within each holding time scenario, higher barrier tarp (large boundary layer) produced higher flux after tarp cut (Table 10). For example, for the 21 d tarping period, the initial post-tarpcut 6 hour cumulative flux was 2.6 ug/cm for 1,3-d as compared to 12.97 ug/cm with a 7 d tarping period.

Phase 2: Analysis of the results from Phase 1 to determine relationships between (1) air gap concentrations and (2) 6- hour and 24-hour volatilization following tarp cutting for the proposed fumigant study

Immediately prior to tarp-cut, the mass of fumigant in the soil-tarp air gap for the 4 cm air gap scenarios was greater than either the 6 hour or 24 hour post-tarp cut volatilized mass simulated immediately after tarp-cutting. However, for the 1 cm air gap scenarios, the mass of fumigant in the soil-tarp air gap represented only 10-20% of the volatilized mass during the 6 or 24 hour post cut period. Thus for the 1 cm air gap scenarios a substantial portion of the post-tarp cut volatilized mass came from upper soil layers. An extended analysis showed strong linear relationships between (a) fumigant masses in the upper soil layers and tarp-soil air gap concentrations, and (b) mass fumigant volatilized in the first periods (6 h or 24 h) after tarp-cutting and fumigant masses in the upper soil layers (Appendix 1). These strong linear relationships demonstrate the physical linkage between sub-tarp fumigant concentrations, mass of fumigant in shallow soil, and flux after tarp-cutting. Based on the high correlation between the three variables we derived a simple relationship directly between post tarp cut volatilization masses and soil-tarp air gap concentrations by regressing volatilization on the soil-tarp air gap concentration for 6 h (Figure 5, y=553x, r2=0.88, p<0.001) and 24 h (Figure 6, y=1115x, r2=0.78, p<0.01). These regressions covered high and low barrier tarps with the associated soil-tarp gap variation, 1,3-d and chloropicrin, and 7 and 21 d holding periods.

To make these empirical relationships more useful, we converted the flux to units of ug/m^{2}s by dividing by the domain width (150cm), converting cm^2 to m^2 and dividing by the respective volatilization times in seconds.

For the 6 hour flux, the regression (Figure 5) and corresponding units-adjusted equations are as follows:

$$Flux(ug / cm, 6h) = 553C(ug / cm3) \quad (1)$$

$$Flux(ug / m2s, 6h) = 1.707C(ug / cm3) \quad (2)$$

For the 24 hour flux (Figure 6), the regression and corresponding units-adjusted equations are as follows:

$$Flux(ug / cm, 24h) = 1114C(ug / cm3) \quad (3)$$
$$Flux(ug / m2s, 24h) = 0.86C(ug / cm3) \quad (4)$$

Phase 3. Post-tarp cutting flux estimation for Lost Hills study and simulation with ISCST3 of near-field air concentrations.

Results from Phase 1 and Phase 2 of this analysis show how to develop a scenario-specific relationship between measured gas concentrations under the tarp (independent variable which can be theoretically measured in the field), and flux upon tarp-cutting (dependent variable). In Phase 3 we describe how to use that predicted flux to estimate upper percentile air concentrations off-field at specified sampling locations using ISCST3, and estimate the probability of obtaining nondetectable concentrations using the Lost Hills study as a model scenario. The general procedure is to:

1. Estimate flux when the tarp is cut based on under-tarp concentrations (performed in Phase 1 and 2).
2. Compile local multi-year meteorological data for a 30 d window around the actual application.
3. Use ISCST3 along with the flux obtained in step 1 and the meteorological data in step 2 to generate a cumulative frequency distribution of air concentrations at the sampler distance from the field.
4. Compare certain percentiles of those air concentrations to human health reference levels.
5. Use the air concentrations obtained in step 3 to estimate the probability of nondetectable concentrations at sampler distance from the field.

Each step outlined above will be discussed in sequence:

Step 1: Estimate flux when the tarp is cut based on soil-tarp air concentrations (performed in Phase 1 and 2).

Equations 2 and 4 developed in Phase 2 provide a method for estimating flux based on the soil-tarp air gap concentrations just before tarp cutting. In the Lost Hills study, tarps were cut from a two acre field on day 5 after fumigation and day 10 after fumigation. The tarp was cut on day 16 after fumigation for the 8 acre field.

The actual field procedure would require measured soil-tarp gap air concentration measurements. However, for illustration, the Hydrus simulated soil-tarp concentrations will be used. Hydrus output included continuous 21-day estimates for soil-tarp air concentrations. From these estimates, soil-tarp gap air concentrations were estimated at 5, 10, and 16d following fumigant application (Table 11). Hydrus simulated soil-tarp concentrations were adjusted to reflect Lost Hills application rates of 221.5 lbs/acre for 1,3-d and 332 lbs/acre for chloropicrin. Equation 2 was applied to these concentrations to estimate a 6 h flux density (Table 11). Only 6 hour average fluxes were used in subsequent calculations in order to illustrate the technique. The 24 hour average fluxes were not used in subsequent calculations.

The Hydrus-estimated soil-tarp air gap concentrations at 5, 10 and 16d ranged from 0.00073 ug/cm^3 to 0.02950 ug/cm^3 (Table 11). These concentrations matched our intuitive expectations in terms of relative magnitude.

- For the high barrier scenarios Hydrus produced higher estimated soil-tarp air gap concentrations than low barrier scenarios.
- The longer holding periods had reduced concentrations.
- Chloropicrin, with a faster degradation rate, had lower concentrations than corresponding 1,3-d scenarios.
- The five day holding period yielded higher flux densities for chloropicrin because the application rate for chloropicrin was higher than 1,3-d. This relationship reversed for 10 and 16d holding periods as the faster chloropicrin degradation dominated.

Step 2: Compile local multi-year meteorological data for a 30d window around the actual application.

To estimate monitored air concentrations at 10m from the field edge, six years of CIMIS met data for station 146 (Belridge in Kern County near Lost Hills) were obtained from an existing database of processed CIMIS data for the dates May 25 – June 24 for 2005-2010 (Vidrio and Johnson 2011). These dates reflected the range of possible dates for fumigant application in the Lost Hills study. This data has been processed for use with ISCST3.

Step 3: Use ISCST3 along with the flux obtained in step 1 and the meteorological data in step 2 to generate a cumulative frequency distribution of air concentrations at the sampler distance from the field.

The ISCST3 control file placed eight receptors evenly around an 8 acre and a 2 acre field at a distance of 10m from field edge to approximate the closest air sampler for the Lost Hills study. For each 31 day period (May 25-June 24) within each year of meteorological data, a simulation was run with the production of 6 hour time weighted averages over the 31d period for each year. This resulted in 8 receptors x 4 six hour periods per day x 31d/year x 6 years=5792 concentration estimates for this time of the year. This set of simulations was repeated for each of the 12 flux estimates in Table 11. Six hour time periods were used because the Lost Hills study protocol required six hour monitoring periods for 2d following tarp cutting and initial application and these post tarp cutting time periods are the most critical. For each flux, these concentration estimates were combined to form a cumulative distribution of 6 hr average concentrations for 2 acre and 8 acre fields. This procedure resulted in 24 cumulative distributions of concentrations. There were 12 flux estimates for each acreage (3 holding periods x 2 chemicals x {high, low barrier tarp}=12) and 2 field sizes (2 acre and 8 acre).

Illustrative ISCST3 derived cumulative distributions for the low barrier, 5 day hold scenario are provided in Figure 7. In this scenario, flux density for 1,3-d was 6.77 ug/m^{2}s and for chloropicrin was 8.22 ug/m^{2}s (Tables 11 and 12). The initial vertical segment at the beginning of each distribution was comprised of concentrations which were estimated by ISCST3 to be zero. For the 8 and 2 acre fields, 26% and 27%, respectively, of the concentrations were estimated by ISCST3 to be zero (Figure 7). With six hour averaging periods, a typical six hour period with a semi-dominant wind direction will be expected to produce some zero concentration monitoring results (Figure 8). The dominant wind direction during 6 a.m. to noon for May 25, 2010 was from the east to the west. The consequent ISCST3-estimated concentrations were maximal on the westernmost receptor at 93 ug/m^3 with zero concentrations on the eastern set of receptors. This six hour period contributes the eight concentration estimates shown in Figure 8 to the cumulative distributions for the two acre field case.

Step 4: Compare certain percentiles of those air concentrations to human health reference levels.

The given human health reference levels were 160 ug/m^3 (24 hour average) for 1,3-d and 203 ug/m^3 (50 ppb, 1-hour average) for chloropicrin. In order to utilize the 6 hour average air concentrations, the health reference levels were adjusted to "equivalent" 6 hour concentrations. This resulted in 320 ug/m^3 for 1,3-d for 6 hours and 342 ug/m^3 for chloropicrin for 6 hours by utilizing a peak to mean scaling relationship described in Barry (2000). The peak-to-mean relationship is not generally used to scale human reference concentrations because toxicological endpoints are to some extent qualitative and may not correlate in a linear way to increases or decreases in exposure time. Nevertheless, the calculation is a consistent method for estimating the concentration equivalency of different time periods and will serve to illustrate the method for six hour exposures.

The percentiles chosen to compare were 90%, 95%, and 99%. Typically high percentiles are chosen for these comparisons in order to provide a conservative context for comparison. It is most desirable if human reference concentrations are higher than most of the projected concentrations. For example, the 90%-tile for the low barrier, 5 day hold for 1,3-d was 71 ug/m^3 (Figure 7). For each of the 12 Lost Hills scenarios, the corresponding cumulative distribution was used to obtain the concentrations corresponding to the listed upper percentiles and compared to the human health reference levels (Table 12).

Certain entries in Table 12 show boldened outlines. These entries correspond to actual treatments in the Lost Hills study. For example, the 5 and 10 day holding periods for 2 acres were studied at Lost Hills. However, there was not a 5 or 10 day holding period for 8 acres. For the two acre fields, the five day hold resulted in exceedance only at the 99th percentile under the high barrier tarp for both 1,3-d and chloropicrin. According to these simulations, the 10 day hold for the two acre fields at this application rate was adequate for either fumigant since no exceedance were predicted even at the 99th percentile. Though not a Lost Hills study case, the 8 acre field is predicted to have exceedances at the 99th percentile for both fumigants for both high and low barrier tarps at five days. In addition, the Hydrus/ISCST3 simulations predict an exceedance at the 95th percentile for chloropicrin under the high barrier tarp at 5 days for the 8 acre field. At 16 days, the two models predict no exceedances at the 99th percentile for either fumigant for either 2 or 8 acres.
Step 5: Use the air concentrations obtained in step 3 to estimate the probability of nondetectable concentrations at sampler distance from the field.

The same cumulative distributions used for estimating human health level exceedances can be used for estimating fraction of nondetects. This estimation focuses on the lower, instead of upper, end of the concentration distributions. The prospective fraction of nondetectable concentrations predicted for the post-tarp cutting monitoring period ranged from a high of 0.89 to a low of 0.40 (Table 13). As discussed earlier, each 6 hour period is likely to exhibit nondetectable concentrations amongst samplers on the upwind side of the field. As the holding time increases, the fraction of predicted nondetects increases because predicted flux density declines due to volatilization through the tarp and degradation in the soil prior to tarp cutting. Field size only had a modest effect on the fraction. For example, for the high barrier tarp with a 16d hold the 1,3-d nondetect fraction was 0.55 and 0.48 for the 2 and 8 acre fields, respectively. With 8 samplers, the expected number of nondetects for the 6 hour period after tarp cut would be 8x0.55=4.4 samples and 3.8 samples for the 2 and 8 acre fields, respectively. The difference between 4.4 and 3.8 is probably statistically undetectable based on field studies. A rough generalization of these nondetect estimates is that half of the samples during the six hour period following tarp cut will likely be nondetects, and that the study will likely produce adequate positive measured concentrations for analysis of flux.

Discussion

The intent of the memorandum was to illustrate a method for estimating flux and resulting air concentrations given daily soil-tarp air gap concentration measurements in order to determine when tarp holding periods were sufficient to avoid the requirement for buffer zones at tarp cutting time. In addition, this work has been oriented towards the Lost Hills fumigant study in order to provide areas where the measured field results can be compared to the Hydrus/ISCST3 simulations results presented herein.

We take up the second area first. There are three areas of comparisons between the calculations in this memorandum and the Lost Hills study: (1) soil-tarp gap concentration measurements, (2) flux during the six hour post-tarp cutting period, and (3) air concentration measurements on the monitors during the six hour post-tarp cutting period. We will also be comparing soil gas concentrations at deeper depths.

All three comparisons will be affected by two important and hard-to-quantify sources of variability: tarp permeability in the field and chemical degradation rate in the soil. While laboratory measurements of tarp permeability provide relatively solid and repeatable estimates for permeability, the application of tarp in a field is a larger-scale process and introduces sources of variability which are excluded in the laboratory. Such sources include tarp perforation (Figure 3), imperfect gluing of adjacent strips, tarp stretching, edge effects, temperature changes, wind turbulence, aging, and precipitation. It is possible that the manufacturing process itself may produce variations in tarp properties. At this time there is no uniform system for identifying tarps beyond specifying the manufacturer and a somewhat loose set of characteristics such as number of layers, thickness, color and perhaps type of resins used in the manufacture of the tarp. Moreover, Papiernik et al. (2010) and the data of Qian et al. (undated) show a substantial effect of humidity upon mass transfer coefficients measured in the laboratory. The Lost Hills DPR study protocol included humidity measurements in the soil-tarp air gap (Tuli 2011) which can be used for comparison to any model results. At this time Hydrus does not have the mechanism to adjust tarp permeability in response to humidity.

The Hydrus simulation for this memorandum used scenarios of contrasting low and high barrier tarps. Our expectation is that the field behavior of the tarps in the Lost Hills study will lie in between the extremes used in the modeling.

The second difficult source of variability is the degradation rate. This is another example of the difficulty in applying refined laboratory measurements to field situations. A recent study indicates a substantial and pervasive sensitivity of maximum flux and cumulative flux to degradation rate (Spurlock et al., 2012). Dungan et al. (2001) found a four-fold decrease in half life for 1,3-d incubated at 40C compared to 20C. In the same article, Dungan et al. (2001) found little effect of soil moisture on degradation over the range of 25% to 75% of water holding capacity. Similar results were determined for chloropicrin, where the degradation rate constant increased nearly an order of magnitude over the temperature range of 20-50C amongst three soils, while soil moisture had minimal impact (Gan et al. 2000). In the case of these two fumigants, temperature appears to have a large effect on degradation while soil moisture does not. There is some evidence of interaction between these fumigants in terms of their degradation rates (Zheng et al. 2003). In most cases, laboratory degradation studies are conducted at constant temperature, whereas shallow soil depths are subject to diurnal temperature variation. Degradation is attributed to abiotic and biotic mechanisms. Biotic mechanisms may cease influence at higher temperatures, whereas abiotic mechanisms continue to respond. These complications and the idiosyncrasies of soil in a particular field at a particular time lead to uncertainties in estimating degradation.

Most fumigant field studies do not attempt to ascertain mass balance because it is difficult. Consequently, even if final soil residues are measured, the missing fumigant can be attributed to volatilization or degradation. These two losses can be misestimated and compensate for each other.

Keeping these formidable difficulties in mind, Hydrus provides a nearly continuous estimation of soil-tarp gap air concentrations. These can be compared directly to the corresponding soil-tarp air gap concentration measurements which have been taken in the Lost Hills study. Flux will be measured/calculated based on the monitored air concentrations for all three fields during the six hour period following tarp cutting. These measured fluxes can be directly compared to the predicted fluxes within this memorandum. The final comparison can be made between the measured air concentrations and the frequency distributions derived from the ISCST3 modeling in conjunction with the Hydrus estimated flux during the post-tarp cut period.

In addition, should these comparisons yield large differences, efforts will be made to understand how these differences arose. A number of environmental measurements were taken such as soil moisture, soil physical properties, temperature and humidity, which can also be compared to Hydrus estimates. These background comparisons may inform the more direct chemical measurement comparisons proposed here.

Generalizing these results

These results can be generalized in a straightforward way. Field size will impact the concentrations. Simulations with ISCST3 can be conducted for a variety of field sizes in order to derive concentration frequency distributions that reflect the size. Meteorology is also a variable and depends largely on what is desired to be represented for regulatory purposes. For example, should a statewide representation be desired, then several meteorological data sets would be utilized from key agricultural areas around the state in order to produce frequency distributions in order to reflect statewide agricultural conditions.

Simulations can also be conducted with ISCST3 which use different time periods such as 3, 4, 6, 8, or 24h. A further refinement might be to use the flux function that more accurately reflects the hourly decline, instead of using the average period flux as was done here.

References

Ajwa, Husein (study director), David Sullivan (Principal Field Investigator), Mike Stanghellini (Fumigant Application), Jonathon Hunzie and CAL/EPA DPR Air monitoring group (Study Monitors and Field QC/QA), Afiqur Khan (Analytical Laboratory Principal Investigator), and Suduan Gao (Soils Analysis and Flux Chamber Studies). 2011. Protocol: Determine emission reduction using totally impermeable film and waiting period for tarp cutting in a large field fumigation trial. Study No. HA2011A Sponsored by USDA-ARS Area-Wide Pest Management Program for Methyl Bromide Alternatives, the California EPA (DPR), and TriCal, Inc.

Ajwa, H., D. Sullivan, M. Stanghellini, W. Ntow, M. Holdsworth, and J. Hunzie. 2009. Volatilization Losses of Methyl Bromide and Chloropicrin from Drip Fumigated Beds Covered with Totally Impermeable Tarp. 2009 Proceedings of 2009 Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions. Available at: <http://mbao.org/2009/Proceedings/Methyl%20Bromide%20Phaseout%20%20Proceedings%20of%202009%20Alternatives%20Research%20Conference.htm>.

Ajwa, Husein. 2008. Testing film permeability to fumigants under laboratory and field conditions. Abstract of Talk presented to MBAO in 2008.

Ajwa, Hussein. 2010. Monitoring of methyl bromide and chloropicrin field emissions from shank applications at shallow and deep injection depths DPR registration data volume 123-0220.

Barry, Terry. 2000. Memorandum to Kean Goh, Ph.D. on Peak-to-mean air concentration estimation for fumigants dated November 6, 2000.

Barry, Terrell and Jing Tao. 2011. Memorandum to Randy Segawa on "Development of flux profiles for new chloropicrin application methods" dated May 18, 2011.

Davidson, Malcolm W.J., Thuy Le Toan, Francesco Mattia, Giuseppe Satalino, Terhikki Maninnen, Maurice Borgeaud. (Undated) On the characterisation of agricultural soil roughness for radar remote sensing studies. Available at: <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.97.9256&rep=rep1&type=pdf>.

DPR (Department of Pesticide Regulation). 2010. The top 100 pesticides used pounds of active ingredients statewide in 2010 (all sites combined). Available at: <http://www.cdpr.ca.gov/docs/pur/pur10rep/top_100_ais_lbs10.pdf>.

Dungan, Robert S., Jianying Gan and Scott R Yates. 2001. Effect of temperature, organic amendment rate and moisture content on the degradation of 1,3-dichloropropene in soil† Pest Manag Sci 57:1107-1113. Available at: <http://www.pw.ucr.edu/textfiles/13D_amendment.pdf>

Gan, J, S.R. Yates, F.F. Ernst, W.A. Jury. 2000. Degradation and volatilization of the fumigant chloropicrin after soil treatment. Journal of Environmental Quality 29(5):1391 1397.
Johnson, Bruce and Frank Spurlock. 2009. Dominant soil types associated with fumigant applications in ozone nonattainment areas (memorandum to Randy Segawa dated January 29, 2009).

Jury, W.A., W.F. Spencer and W.J. Farmer. 1986. Behavior Assessment Model for Trace Organics in Soil: I' Model Description. J. Env. Qual 12:558-564.

Leij, F.J., W.J. Alves, M.Th. van Genuchten, and J.R. Williams. 1996. Unsaturated Soil Hydraulic Database. UNSODA v. 1.0. U.S. Salinity Laboratory, Riverside, California. Available at: <http://www.ars.usda.gov/Services/docs.htm?docid=8967>.

Matthias,A.D., A. Fimbres, E. E. Sano, D. F. Post, L. Accioly, A. K. Batchily, and L. G. Ferreira. 2000. Surface Roughness Effects on Soil Albedo. Soil Sci. Soc. Am. J. 64:1035–1041

Papiernik, S.K., F.F. Ernst, and S.R. Yates. 2002. An apparatus for measuring the gas permeability of films. J. Environ. Qual. 31:358-361.

Papiernik, Sharon K., S.R. Yates and Jianying Gan. 2001. An approach for estimating the permeability of agricultural films. Environmental Science and Technology 35(6):1240-1246.

Papiernik, Sharon K., Scott R. Yates and Daniel O. Chellemi. (2010). A standardized approach for estimating the permeability of plastic films to soil fumigants under various field and environmental conditions. JEQ Volume 39. Published online 13 Sept 2010.

Qian, Yaorang, Alaa Kamel, Chuck Stafford, Thuy Nguyen and Scott Yates. (undated) Film Permeability Determination Using Static Permeability Cells.

Rahman, M.M., M.S. Moran, D.P. Thoma, R. Bryant, C.D. Holifield Collins, T. Jackson, B.J. Orr, M. Tischler. 2008. Mapping surface roughness and soil moisture using multi angle radar imagery without ancillary data. Remote Sensing of Environment 112 (2008) 391B402.

Šimůnek, Jiri. (Undated). HYDRUS-1D and HYDRUS (2D/3D) Modifications to Simulate and Analyze the Transport of Fumigants. Department of Environmental Sciences University of California Riverside Riverside, CA 92521 Agreement No 09-C0078 Department of Pesticide

Regulation Environmental Monitoring Brach[sic] 1001 I Street 4th Floor Sacramento, California 95814.

Šimůnek, J., M. Šejna, and M. Th. van Genuchten, 2007. The HYDRUS Software Package for Simulating Two- and Three-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media, User Manual, Version 1.0, PC Progress, Prague, Czech Republic, pp. 161.

Spurlock, F. 2009. Memorandum to Randy Segawa on "Fumigant Transport Modeling Using HYDRUS: 2. Comparison of Model Simulations to Analytical Solutions of Fick's Second Law of Diffusion" dated August 26, 2009.

Spurlock, Frank, Rick Bergin, Atac Tuli, and Bruce Johnson. 2010. Memorandum to Randy Segawa on FUMIGANT TRANSPORT MODELING USING HYDRUS: 4. DEVELOPMENT AND TESTING OF MODIFICATIONS TO ENHANCE FUMIGANT FIELD SIMULATIONS dated May 6, 2010.

Spurlock, Frank. 2008. Memorandum to Randy Segawa on Fumigant Transport Modeling with Hydrus: Estimation of soil hydraulic parameters using pedotransfer functions dated August 14, 2008.

Spurlock, Frank. 2008. Memorandum to Randy Segawa on Fumigant Transport Modeling with Hydrus: Estimation of soil hydraulic parameters using pedotransfer functions dated August 14, 2008. Available at: <http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/2066_rosetta.pdf>.

Spurlock, Frank. 2010. Memorandum to Randy Segawa on Fumigant transport modeling using Hydrus: 3. Selection, temperature dependence and sensitivity analysis of fumigant physicochemical properties dated 2.1.2010 Revision.

Spurlock, F., J. Šimůnek, B. Johnson, and A. Tuli. 2012. Sensitivity Analysis of Vadose Zone Fumigant Transport and Volatilization. Submitted to JEQ.

Tuli, Atac. 2011. STUDY 273: MODELING AND MONITORING FIELD EMMISIONS OF FUMIGANTS UNDER TOTALLY IMPERMEABLE FILMS (TIF) Protocol dated May 2011 (final version).

van Genuchten, M. Th. 1980. A Closed-form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils. Soil Sci. Soc. Am. J., 44:892-898.

Vidrio, Edgar and Bruce Johnson. 2011. PART 1: DATABASE CREATION OF ISCST3-READY FILES PREPARED FROM CIMIS METEOROLOGICAL NETWORK DATA. July 2011. California Environmental Protection Agency Department of Pesticide Regulation Environmental Monitoring Branch Air Program P.O. Box 4015 Sacramento, California 95812-4015. Available at: <http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/cimis_weather_data_preparations.pdf>.

Zheng, W., Papiernik, S.K., Guo, M., Yates, S.R. 2003. Competitive Degradation Between the Fumigants Chloropicrin and 1,3 Dichloropropene in Unamended and Amended Soils. Journal of Environmental Quality. 32:1735 1742.

Figure 1. Bedded tarp. Tarp stretched over dirt clod center right.

Figure 2 Bedded tarped application (DPR photo archives).

Figure 3. Blown up section from lower portion of right hand bed from Arrows point towards possible small punctures in tarp.

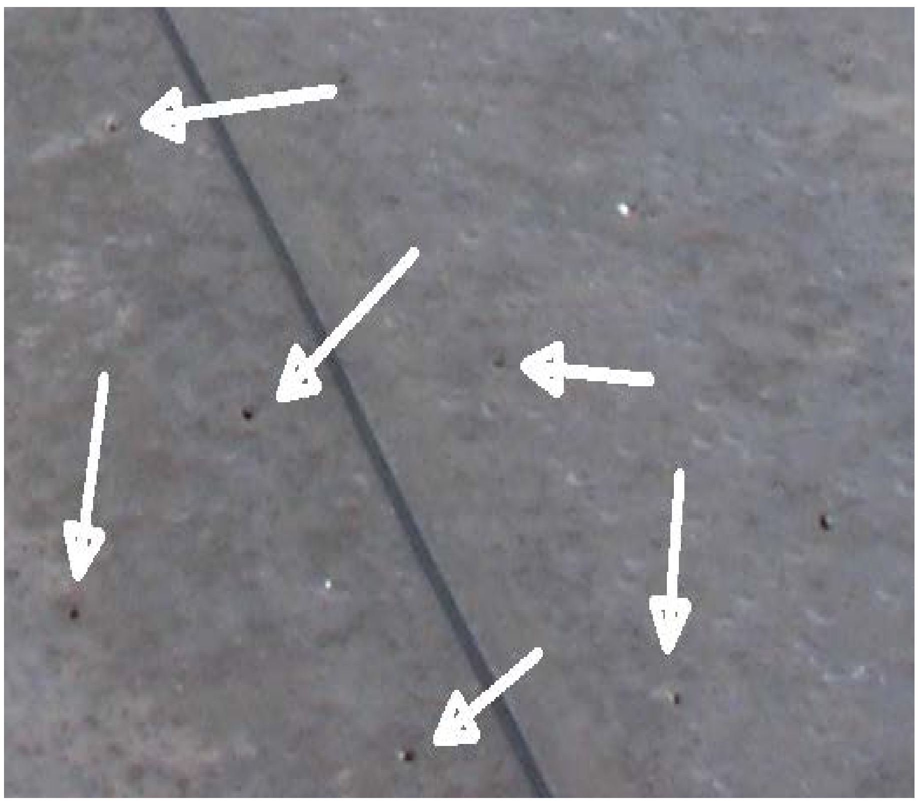
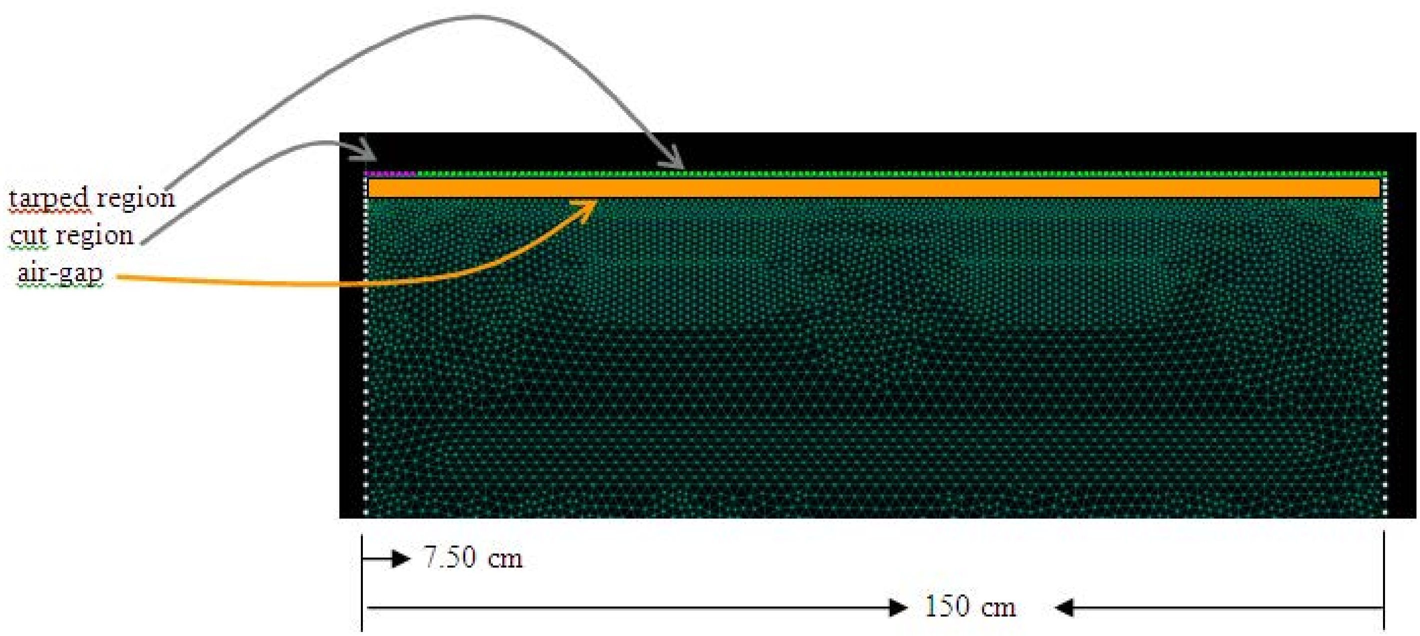


Figure 4. Top of modeling domain in second stage simulation illustrating size and location of tarp-cut area at soil surface



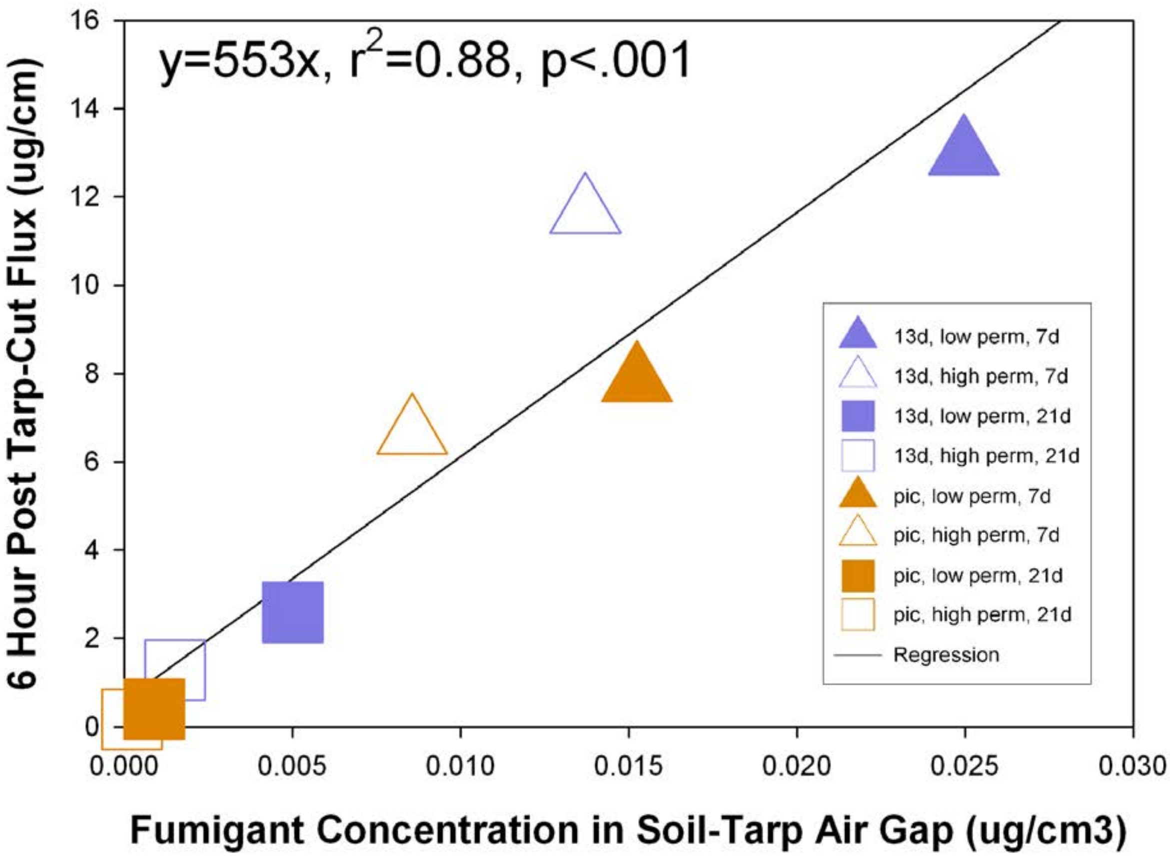


Figure 5. 6 hour cumulative flux as a function of soil-tarp air gap concentration.

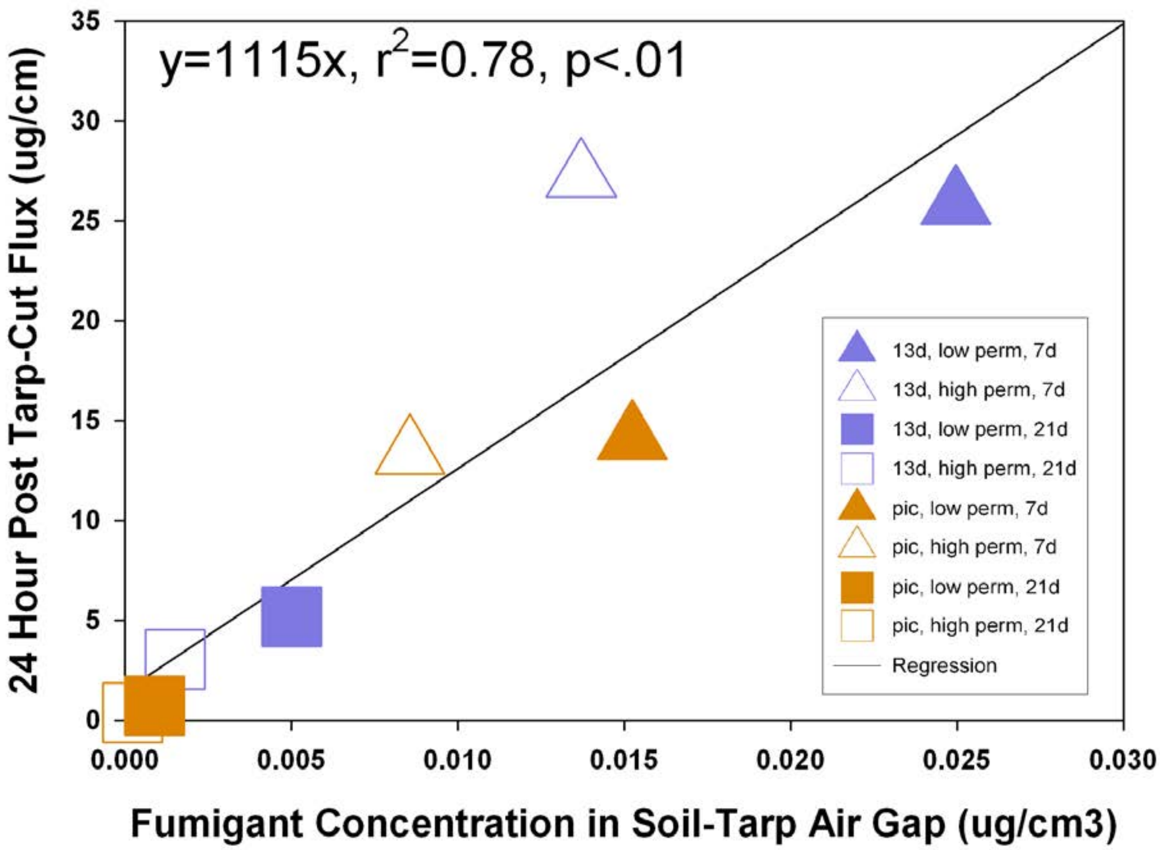


Figure 6. 24 hour cumulative flux as a function of soil-tarp air gap concentration.

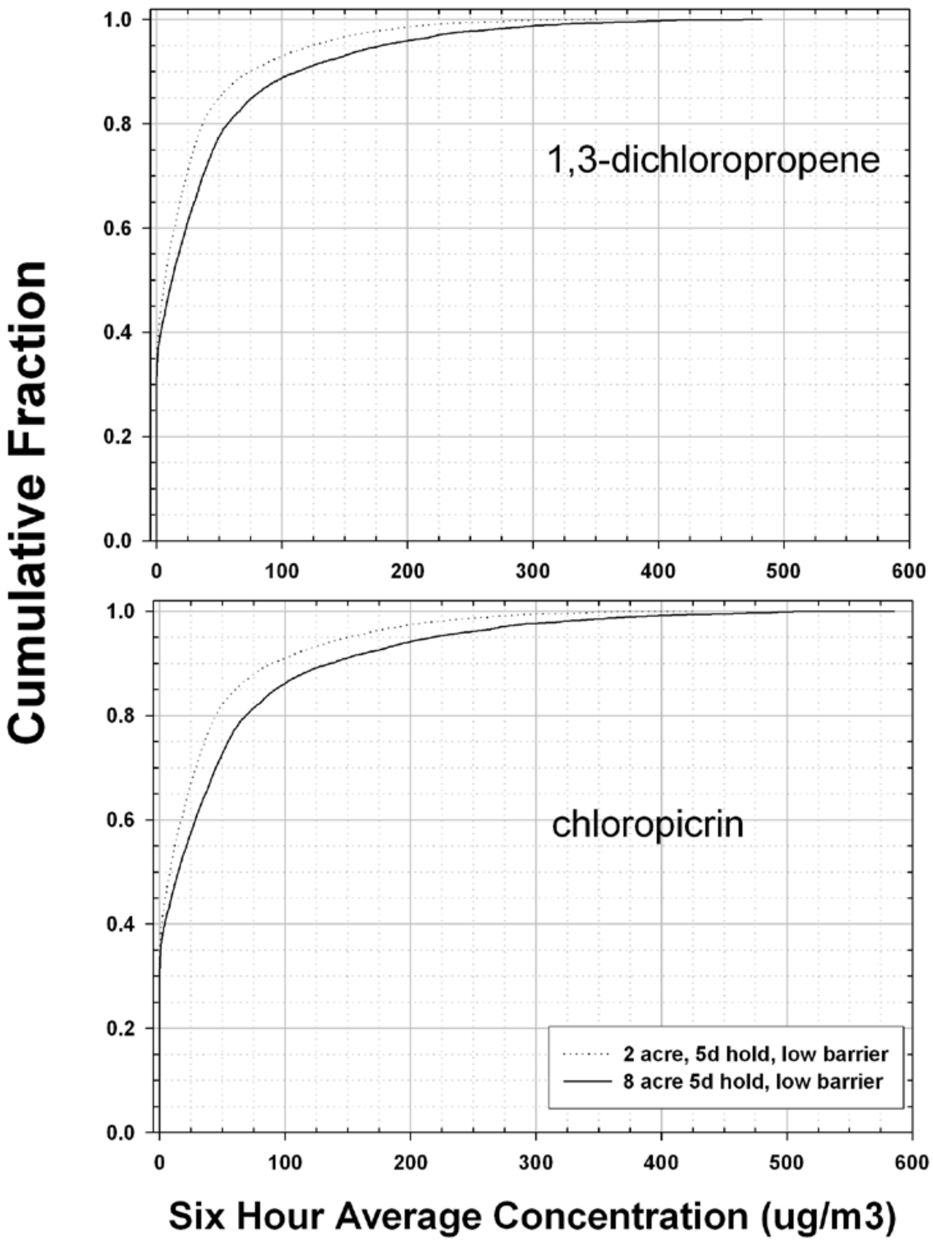


Figure 7. Illustrative cumulative concentration distributions for 1,3-d and chloropicrin for 5 day hold, low barrier tarp for 2 and 8 acres. Associated flux densities were 6.77 ug/m2s and 8.22 ug/m2s for 1,3-d and chloropicrin.

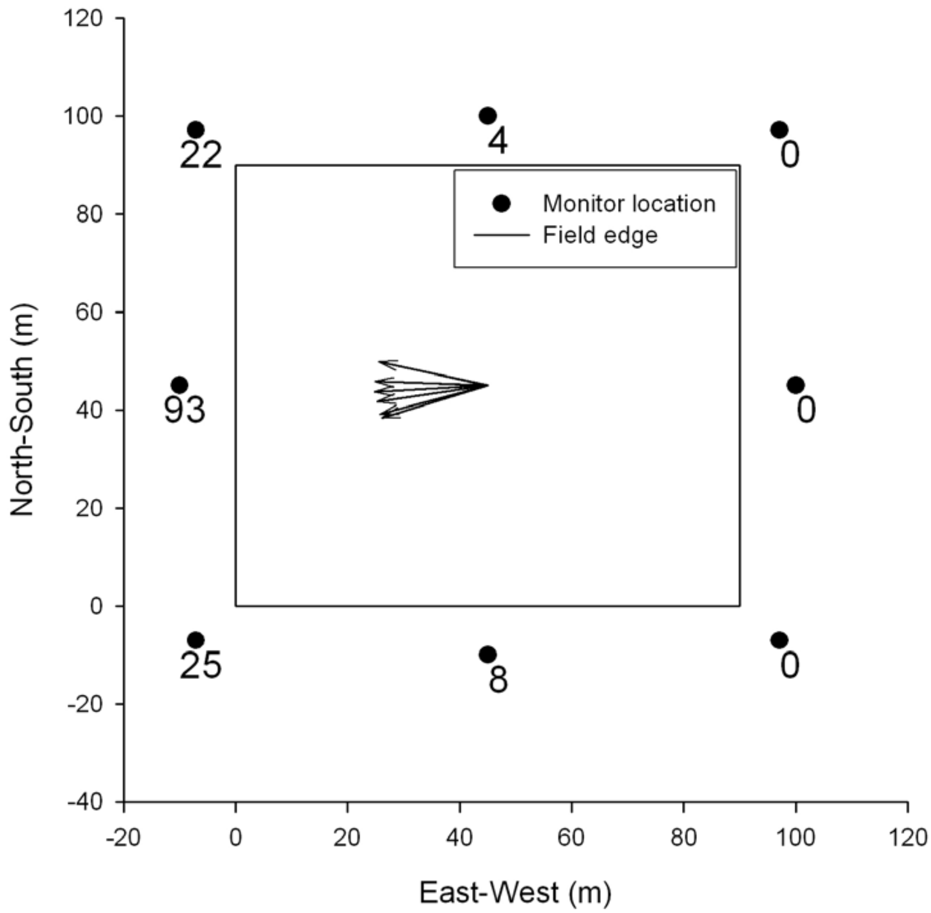


Figure 8. Example period calculation for two acre field (6AM to 12 Noon 5/25/2010) with concentration labels in ug/m3 at each of eight receptors and six arrows showing the "to" wind directions for the six hours.

Table 1. Surface roughness measurements. RMS=root mean square and is a measure of the height.

Field Description	RMS (cm)	Comments	Source
ploughed	2 to 5	most rough, sandy clay loam or clay loam	Davidson et al. (undated from Figure 3)
rough Harrowed	1 to 3	less rough, sandy clay loam or clay loam	Davidson et al. (undated from Figure 3)
smooth Harrowed	0.5 to 1.5	more smooth, sandy clay loam or clay loam	Davidson et al. (undated from Figure 3)
rolled	0.5 to 1.5	most smooth, sandy clay loam or clay loam	Davidson et al. (undated from Figure 3)
non-ag, semi-arid	0.48 to 1.3	gravelly sandy loam	Rahman et al. (2008)
rough plowed	~3.0	Gila fine sandy loam	Matthias et al. (2000, Figure 3b)
rough plowed	3.5 to 3.75	Pima Clay loam	Matthias et al. (2000, Figure 3b)
disked	2.0 to 2.25	Gila fine sandy loam	Matthias et al. (2000, Figure 3b)
disked	~2.0	Pima Clay loam	Matthias et al. (2000, Figure 3b)
disked-disked	1 to 1.4	Gila fine sandy loam	Matthias et al. (2000, Figure 3b)
disked-disked	~1.6	Pima Clay loam	Matthias et al. (2000, Figure 3b)
seedbed	1.6 to 1.8	Gila fine sandy loam	Matthias et al. (2000, Figure 3b)
seedbed	1.6 to 1.8	Pima Clay loam	Matthias et al. (2000, Figure 3b)

Table 2. Mass transfer coefficients (cm/h) for various tarps for 1,3-D and chloropicrin (after Ajwa 2008)

Film Type	Cis 1,3-D Before	Cis 1,3-D After	Trans 1,3-D Before	Trans 1,3-D After	Chloropicrin Before	Chloropicrin After
Pliant black embossed, 1.25 mil	14.61	16.38	17.32	18.22	9.04	9.98
PolyPak Std, 1.5 mil	3.23	3.79	5.16	5.65	1.49	1.70
Poly Pak SIF, 2.0 mil	1.42	1.53	1.51	1.71	0.67	0.72
Micro-embossed (Blockade), 1.25 mil)	0.86	0.88	1.65	1.74	0.11	0.17
Bromostop VIF (1.38 mil)	0.07	0.27	0.09	0.41	0.02	0.18
Eval/Mitsui film (1.38 mil) (TIF)	0.001	0.02	0.001	0.07	0.001	0.01

Table 3. Summary MTCs (cm/h) for VIF tarps (n=18) for 1,3-D and chloropicrin (Papiernik et al. 2010).

	Cis 1,3-D	Trans 1,3-D	Chloropicrin
Mean	0.00535	0.01182	0.00022
Median	0.00361	0.00833	0.00008
St Dev	0.00506	0.01048	0.00038
Max	0.01724	0.03704	0.00138
Min	0.00068	0.00172	0.00001

Table 4 MTCs (cm/h) for TIF tarps (n=9) estimated by USEPA (Qian personal communication) ambient humidity			
	Cis 1,3-D	Trans 1,3-D	Chloropicrin
Mean	0.000211	0.000333	0.000178
Median	0.000200	0.000300	0.000200
St Dev	0.000242	0.000320	0.000217
Min	0	0	0
Max	0.000800	0.001100	0.000700

Table 5 MTCs (cm/h) for TIF tarps (n=9) estimated by USEPA (Qian personal communication) high humidity.

	Cis 1,3-D	Trans 1,3-D	Chloropicrin
Mean	0.0556	0.0941	0.0123
Median	0.0250	0.0382	0.0029
St Dev	0.0852	0.1569	0.0244
Min	0.0013	0.0013	0
Max	0.2745	0.5024	0.0758

Table 6. Fumigant physicochemical properties[A, B]

[A] 1,3-dichloropropene data is average of *cis*- and *trans*- isomers

Property	1,3-dichloropropene	chloropicrin
D_g, diffusion coefficient in air ($cm^2\ day^{-1}$)	6886	6515
D_w, diffusion coefficient in water ($cm^2\ day^{-1}$)	0.735	0.707
K_d, soil-water distribution coefficient ($cm^3\ g^{-1}$)	0.03	0.03
K_h, air-water partition coefficient (dimensionless)	0.060	.0825
k_1, first-order soil degradation coefficient (day^{-1})	0.099	0.198
D_gE_a, D_g activation energy ($J\ K^{-1}\ mol^{-1}$)	18035	18035
D_wE_a, D_w activation energy ($J\ K^{-1}\ mol^{-1}$)	4560	4566
K_hE_a, K_h activation energy ($J\ K^{-1}\ mol^{-1}$)	32085	39273

[B] The activation energy terms are used in HYDRUS to describe the temperature dependence of the parameter of interest using an Arrhenius-type relationship (Šimůnek et al., 2007)

Table 7 Eight scenarios simulated with Hydrus 2D/3D.

	Stage 1			
Fumigant	Air Gap	Boundary Layer	Holding Time	Stage 2
1,3-D	4 cm	57000 cm	7 d	Tarp Cut (3.5 d)
1,3-D	1 cm	500 cm	7 d	Tarp Cut (3.5 d)
1,3-D	4 cm	57000 cm	21 d	Tarp Cut (3.5 d)
1,3-D	1 cm	500 cm	21 d	Tarp Cut (3.5 d)
Chloropicrin	4 cm	57000 cm	7 d	Tarp Cut (3.5 d)
Chloropicrin	1 cm	500 cm	7 d	Tarp Cut (3.5 d)
Chloropicrin	4 cm	57000 cm	21 d	Tarp Cut (3.5 d)
Chloropicrin	1 cm	500 cm	21 d	Tarp Cut (3.5 d)

Table 8 Stage 1 scenarios and associated soil-subregions.

Stage 1 Scenarios and soil subregions			
4 cm airgap, boundary layer 57000 cm			
Subregion Number	Depth range below surface	Observation node depth	Node Number
1	0 cm to 4 cm	2 cm	1512
2	4 cm to 15 cm	10 cm	3787
3	15 cm to 25 cm	20 cm	7527
4	25 cm to 35 cm	30 cm	4655
5	35 cm to 45 cm	40 cm	3118
6	45 cm to 65 cm	55 cm	7030
7	65 cm to 150 cm	105 cm	8578
Q:\baseline-studies\tarp-split-aircon-est\[subregions.xls]Sh			
1 cm air gap, boundary layer 500 cm			
Subregion Number	Depth range below surface	Observation node depth	Node Number
1	0 cm to 1 cm	0.5 cm	1513
2	1 cm to 11 cm	6 cm	3388
3	11 cm to 21 cm	16 cm	5969
4	21 cm to 31 cm	26 cm	6530
5	31 cm to 41 cm	36 cm	237
6	41 cm to 61 cm	51 cm	3116
7	61 cm to 150 cm	105 cm	8578

Table 9. Basic Hydrus modeling results for simulated pre-tarp-cut holding periods.

Fumigant	Letter designation	Boundry Layer (cm)	Air Gap (cm)	Pre-Cut Duration (d)	Total Mass Applied to Modeling Domain (ug/cm)	Total Mass Applied as Rate Per Surface Area (ug/cm2)	Total Mass (ug/cm) degraded 7d or 21d	Total Mass (ug/cm) volatilized 7d or 21d	Total Mass (ug/cm) remaining in soil 7d or 21d	Total Mass sum at 7d or 21d (ug/cm)	Percent Mass Error
13d	1C2	57400	4	7	1739	11.59	872.86	2.32	867.91	1743.09	0.26
13d	1C3	500	1	7	1739	11.59	834.76	158.06	750.64	1743.46	0.29
13d	1C4	57400	4	21	1739	11.59	1525.60	4.92	215.90	1746.42	0.47
13d	1C5	500	1	21	1739	11.59	1335.70	272.10	140.09	1747.89	0.55
pic	1C2	57400	4	7	1739	11.59	1315.10	2.30	433.64	1751.04	0.72
pic	1C3	500	1	7	1739	11.59	1245.10	151.56	355.47	1752.13	0.79
pic	1C4	57400	4	21	1739	11.59	1724.90	3.35	27.46	1755.70	0.99
pic	1C5	500	1	21	1739	11.59	1547.00	193.35	15.99	1756.34	1.03

Table 10. Targeted Hydrus modeling results. Air concentrations occur at the end of the Part 1 simulation, after either 7d or 21d holding period.

					From Part 1 - pre tarp cut				From Part 2 - post tarp cut	
Fumigant	Letter designation	Boundry Layer (cm)	Air Gap (cm)	Pre-Cut Duration (d)	Mass in top 5 cm before tarp cut (ug/cm)	Concentration in Soil-Tarp Air Gap (ug/cm3 air)	Concentration in Soil Air of Soil Layer Below Gap (ug/cm3 air)		Cumulative flux after 6 hours (ug/cm)	Cumulative flux after 24 h (ug/cm)
13d	1C2	57400	4	7	37.06	0.02496	0.01702		12.97	25.84
13d	1C3	500	1	7	25.45	0.01371	0.01212		11.64	27.17
13d	1C4	57400	4	21	7.41	0.00501	0.00326		2.60	5.16
13d	1C5	500	1	21	2.80	0.00150	0.00134		1.29	3.02
pic	1C2	57400	4	7	20.41	0.01524	0.01073		7.83	14.06
pic	1C3	500	1	7	11.32	0.00856	0.00722		6.64	13.31
pic	1C4	57400	4	21	1.04	0.00088	0.00051		0.40	0.72
pic	1C5	500	1	21	0.29	0.00023	0.00018		0.17	0.35

Table 11. Estimated average 6 hour flux densities for the Lost Hills study based on Hydrus-estimated soil-tarp air gap concentrations. Hydrus concentrations adjusted by Lost Hills application rates of 222 lbs/acre for 1,3-d and 332 lbs/acre for chloropicrin and Hydrus equivalent application rate of 1.034 lbs/acre. For example, Field 3, low barrier Hydrus-estimated 1,3-d concentration of 0.01850 ug/cm3 is multiplied by 214.25 (=222/1.034) yielding 3.964 ug/cm3 for the estimated field concentration. The flux density is based on equation 2 for 6 hour average flux density. For example, 3.964 ug/cm3 x 1.707=6.766 ug/m2s.

Chemical	Lost Hills Field Number	Holding Time (Days)	Tarp Barrier	Hydrus estimated tarp gap concentration (ug/cm3)	Estimated Field Concentration (ug/cm3	Estimated 6 h Flux Density (ug/m2s)
1,3-D	Field 3	5	Low	0.01850	3.964	6.766
			High	0.02950	6.320	10.789
	Field 2	10	Low	0.00837	1.793	3.061
			High	0.01800	3.857	6.583
	Field 1	16	Low	0.00320	0.686	1.170
			High	0.00891	1.909	3.259
Chloropicrin	Field 3	5	Low	0.01500	4.817	8.223
			High	0.02578	8.277	14.130
	Field 2	10	Low	0.00368	1.181	2.017
			High	0.00893	2.867	4.894
	Field 1	16	Low	0.00073	0.236	0.402
			High	0.00238	0.765	1.306

Table 12. Predicted exceedance ranges for Lost Hills study using relationships based on Hydrus simulation and adjusted to application rates of 221.5 lbs /acre and 332.0 lbs/acre active ingredient for 1,3-d and chloropicrin, respectively. Shaded squares denote six-hour time weighted concentrations which exceed 320 ug/m3 and 342 ug/m3 for 1,3-d and chloropicrin, respectively. Boxed cells represent cases in the Lost Hills study and will be compared to monitoring results.

				Two acre field			**Eight acre field**		
				Concentration Cutpoint (ug/m3 - 6 hours) for All Concentrations (includes zero concentrations)			Concentration Cutpoint (ug/m3 - 6 hours) for All Concentrations (includes zero concentrations)		
	Hold time (d)	tarp barrier	Estimated Flux (ug/m2s)	90th	95th	99th	90th	95th	99th
1,3-d	5	low	6.77	71	120	244	106	176	339
	5	high	10.79	113	191	389	169	281	540
	10	low	3.06	32	54	110	48	80	153
	10	high	6.58	69	117	237	103	171	330
	16	low	1.17	12	21	42	18	30	59
	16	high	3.26	34	58	118	51	85	163
chloropicrin	5	low	8.22	86	146	297	129	214	412
	5	high	14.13	148	250	509	221	368	707
	10	low	2.02	21	36	73	32	53	101
	10	high	4.89	51	87	176	77	127	245
	16	low	0.40	4	7	15	6	10	20
	16	high	1.31	14	23	47	20	34	65

Table 13. Predicted fraction of nondetectable post-tarp cutting concentrations for Lost Hills study using relationships based on Hydrus simulation and adjusted to application rates of 221.5 lbs /acre and 332.0 lbs/acre active ingredient for 1,3-d and chloropicrin, respectively. Detection limit was 0.2 ug. Pump rate was 100ml/min. Boxed cells represent cases in the Lost Hills study and will be compared to monitoring results.

				Estimated Nondetect Fraction	
	Hold time (d)	**Tarp Barrier**	**Estimated Flux Density (ug/m2s)**	**Two acre field**	**Eight acre field**
1,3-d	5	low	6.77	0.45	0.40
	5	high	10.79	0.45	0.40
	10	low	3.06	0.55	0.48
	10	high	6.58	0.45	0.40
	16	low	1.17	0.76	0.65
	16	high	3.26	0.55	0.48
chloropicrin	5	low	8.22	0.45	0.40
	5	high	14.13	0.42	0.38
	10	low	2.02	0.63	0.54
	10	high	4.89	0.50	0.44
	16	low	0.40	0.89	0.83
	16	high	1.31	0.73	0.63

Appendix 1:**Extended analysis between fumigant masses in the upper soil layers and tarp-soil air gap concentrations and between volatilization and fumigant masses in the upper soil layers**

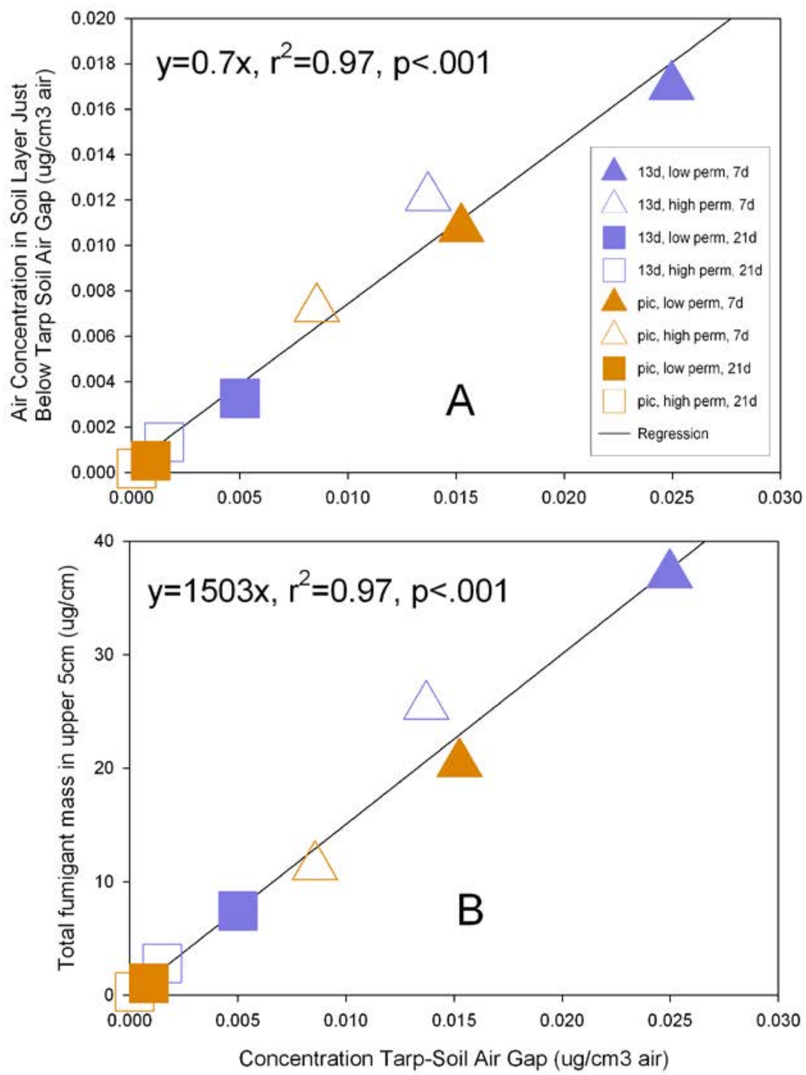
The difference between this analysis and the one in the body of the memorandum is that in this analysis a relationship is first established between the soil-tarp air gap concentration and the mass in the top 5 cm of the soil (which includes either the 4- or 1- cm soil-tarp air gap, plus a portion of the underlying soil layer in order to give a 5 cm depth). Then a relationship is established between 6- and 24 hour flux and the mass in the top 5 cm of the soil.

The reason for this analysis was to assure ourselves that the source of the fumigant, both the soil-tarp air gap and the underlying soil layer were all related. The simulation utilized either a 1 cm or 4 cm soil-tarp air gap. We will refer to the soil layer below this air gap as the soil layer below the soil-tarp air gap. The mass in the top 5 cm refers to the mass of fumigant in the soil-tarp air gap plus a fraction of the mass in the bulk soil layer below the soil-tarp air gap. The fraction was determined to be either 1/11 in the case of the 4 cm soil-tarp air gap and 4/10 in the case of the 1 cm soil-tarp air gap, where the denominator was the width of the soil layer below the soil-tarp air gap and the numerator was the number of centimeters required to produce a 5 cm depth starting from the top of the tarp.

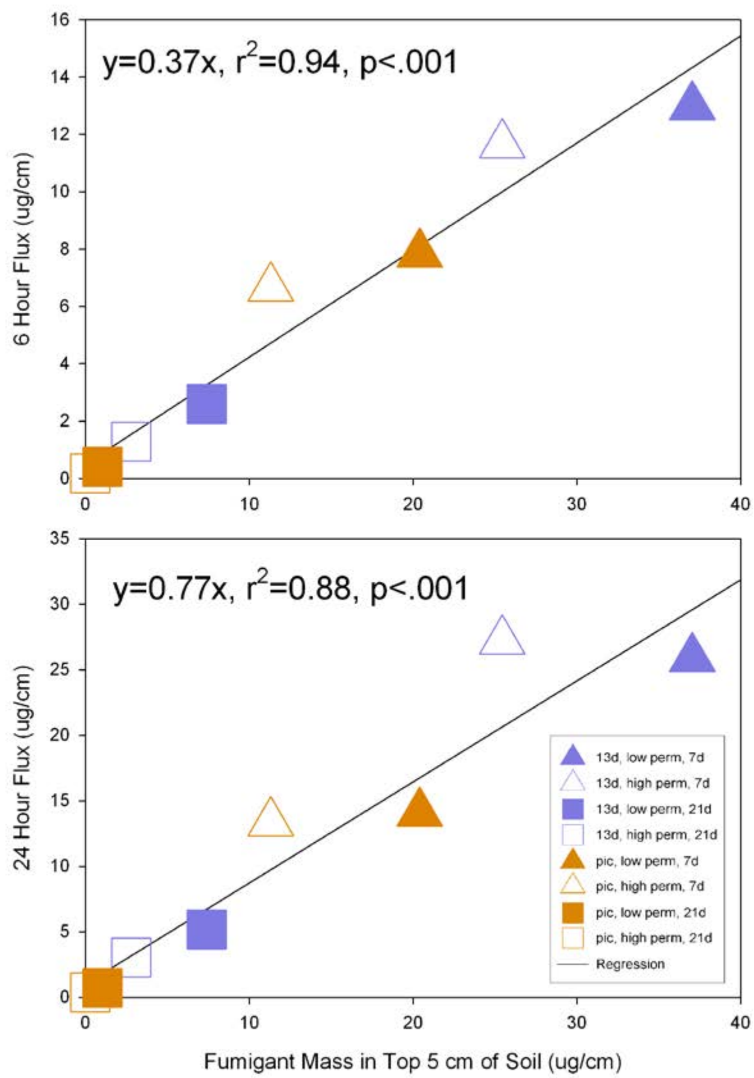
There was a strong relationship between fumigant concentration in the soil in the layer below the soil-tarp air gap and the concentration of the fumigant in the soil-tarp air gap (y=0.7x (r2=0.97, p<.001, Appendix 1 Figure 1A). On average this concentration in the lower layer was about 0.7 of the concentration in the soil-tarp air gap. Consequently, any proportional relationship established with the soil-tarp air gap concentration will automatically reflect a proportional relationship with the soil air concentration in the layer immediately below the soil-tarp air gap. This is important since these two air volumes are probably the most immediate sources of atmospheric volatilization when the tarp is cut.

The second regression utilizes the total fumigant mass in the upper 5 cm of soil (ug/cm) as the y value versus the air concentration in the top layer (ug/cm3) as x. The regression was strong with y=1503x (r2=0.97, p<.001, Appendix 1 Figure 1B). The intercept was negligible and nonsignificant. The mass in the upper 5 cm of soil is defined as the total mass for the modeling domain in the upper 5 cm including the soil-tarp air gap. The relationship between the fumigant mass in the upper 5 cm and the concentration in the soil-tarp air gap holds over the 8 scenarios, which include the two fumigants, 2 holding periods and 2 tarp permeabilities. This key relationship reflects the underlying partitioning between soil/gas/liquid at the moment before tarp cutting.

The third and fourth regressions relate the total flux 6 hours and 24 hours after tarp split to the fumigant mass in the top 5 cm of the soil (Appendix 1 Figure 2). The relationship was a bit stronger for the 5 hour flux with $y=0.37x$ ($r2=0.94$, $p<.001$) than the 24 hour flux ($y=0.77x$, $r2=0.88$, $p<.001$). In both cases the y intercept was small and non-significant. The volatilization mass used in these regressions is an absolute amount for this simulation reflecting the simulation application rate and the size of the simulation domain. In order to generalize these relationships, both the top 5 cm soil mass and the amount volatilized need to be divided by the width of the simulation domain, which was 150cm.



Appendix 1 Figure 1. (A). Regression of concentration in soil layer below gap (y) to concentration in soil-tarp gap (x). Intercept small and non-significant. (B) Regression of fumigant mass in upper 5 cm (gap + portion of adjacent soil layer) (y) vs concentration in tarp-soil gap (x). Intercept small and non-significant. The below-tarp measurement of air concentration is a strong indicator of mass in the top 5 cm.



Appendix 1 Figure 2. Relationship between 6- and 24-hour post-tarp cut cumulative flux and fumigant mass in top 5 cm of soil. For both regressions, intercept small and not statistically significant.

Development and linkage of equations

Top 5 cm fumigant mass vs. upper soil air concentration (Appendix 1 Fig 1B).

$$M5 = 1503 * C \qquad \text{A (5)}$$

Where M5= is the total mass in the top 5 cm of the modeling domain (ug/cm) and C is the air concentration in the top layer (ug/cm3).

Divide the right side by 150 cm, the horizontal length of the modeling domain. This results in

$$MA5 = 10 * C \qquad \text{A (6)}$$

Where now MA5 is the mass per surface area (ug/cm2) in the top 5 cm of soil.

6 hour flux vs. mass in top 5 cm (Figure 6A)

$$F6 = 0.37 * M5 \qquad \text{A (7)}$$

Where F6 is the total volatilized mass loss from the soil in during the first 6 hours following tarp cut (ug/cm). The mass on both sides reflects the specific length of the modeling domain, so divide both sides by 150 cm in order to put the mass on a per area basis. This results only in a change of variable names and units.

$$FA6 = 0.37 * MA5 \qquad \text{A (8)}$$

Where now FA6 is ug/cm2 volatilized over the 6 hours. Common units for volatilization and useful for ISC are ug/m2s. To convert FA6 into these units, first convert cm2 to m2, then convert 6 hours to seconds. Starting with the desired units, this conversion is

$$UFA6\left(\frac{ug}{m^2 s}\right) = FA6\left(\frac{\frac{ug}{cm^2}}{\text{"}6hour\ period\text{"}}\right) * \left(\frac{1E4cm^2}{m^2}\right) * \left(\frac{1}{3600\frac{s}{h} * \frac{6h}{\text{"}6h\ period\text{"}}}\right) = 0.463 * FA6 \qquad \text{A (9)}$$

Combining equations 4 and 5 gives

$$UFA6(\frac{ug}{m^2 s}) = 0.1713 * MA5 \quad \text{A (10)}$$

Equation 6 predicts the average flux over 6 hours in ug/m2s based on the area-normalized mass (ug/cm2) in the top 5 cm of the soil.

24 hour flux vs. mass in top 5 cm

The procedure is nearly the same as the 6 hour procedure.

$$UFA24(\frac{ug}{m^2 s}) = FA24(\frac{\frac{ug}{cm^2}}{\text{"}24h\ period\text{"}}) * (1E4\frac{cm^2}{m^2}) * (\frac{1\,day}{3600\frac{s}{h} * \frac{24h}{\text{"}24h\ period\text{"}}}) = 0.1157 FA24 \quad \text{A (11)}$$

Where UFA24 is the average 24 hour flux density (ug/m2s) and FA24 (ug/cm2) is the area normalized mass flux during the 24 hour period following tarp cutting. This is related to the area normalized mass in the top 5 cm as

$$\begin{aligned} &FA24 = 0.77 MA5 \\ &so\ that \\ &UFA24(\frac{ug}{m^2 s}) = 0.1157 * FA24 = 0.1157 * (0.77 * MA5) = 0.0891 * MA5 \end{aligned} \quad \text{A (12)}$$

The final step is to substitute the top layer air concentration for MA5 from equation 2. This final substitution relates the flux to the top layer soil air concentration just before tarp cutting.

For 6 hours,

$$UFA6(avg6hrflux\ ug/m2s) = 0.1713 * (10 * C) = 1.713 * C(belowtarpconc\ ug/cm3) \quad \text{A (13)}$$

And for 24 hours

$$UFA24(avg24hflux\ ug/m2s) = 0.0891(10 * C) = 0.891 * C \quad \text{A (14)}$$

These equations compare favorably with the more directly obtained equations 1 and 2 which had multiplicative coefficients of 1.707 and 0.86 for 6h and 24h, respectively.