

Department of Pesticide Regulation



Brian R. Leahy Director

MEMORANDUM

Edmund G. Brown Jr. Governor

- TO: Randy Segawa Environmental Program Manager I Environmental Monitoring Branch 916-445-3870
- FROM: Frank Spurlock, PhD Research Scientist III Environmental Monitoring Branch 916-324-4124

Original Signed by R. Segawa for F. Spurlock

DATE: June 3, 2014

SUBJECT: HYDRUS ESTIMATES OF CUMULATIVE 1,3-DICHLOROPROPENE AND CHLOROPICRIN EMISSIONS FROM LOW PERMEABILITY TARP STRIP APPLICATIONS

INTRODUCTION

This report describes HYDRUS 2D/3D simulations for estimating cumulative emissions from deep strip 1,3-dichloropropene (13D) and chloropicrin (PIC) applications under totally impermeable film tarps (TIF). The simulations use measured soil and environmental data from the recent Lost Hills fumigation study (Tuli, 2011), and the calibrated TIF and fumigant properties determined in that study (Spurlock et al., 2013a).

In the Lost Hills study, Spurlock et al. (2013b) concluded that, once properly calibrated, HYDRUS accurately simulated individual heat transport, water transport, and fumigant partitioning and degradation processes. The HYDRUS model also yielded 13D and PIC cumulative flux and maximum discrete time-average flux density estimates that were within the range of uncertainty of flux estimates derived from conventional inverse ISCST3 modeling (Spurlock et al., 2013b).

METHODS

Modeling Scenarios

Strip applications are typically used in orchard pre-plant situations for nematode control. Common application geometries are 5 to 7 shanks spaced $20^{\circ} - 24^{\circ}$ apart, with injection depths in the range of $18^{\circ} - 24^{\circ}$ (M. Stanghellini, personal communication). TIF strip applications will consist of 11' wide treated strips separated by untreated strips. The treated strip is covered by a 13' wide TIF tarp, with 1' of the tarp "tucked" into the soil to approximately 10" depth on each side. The proportion of treated area to the entire field area varies with the tree type to be planted; 60% was used in the scenarios here. Three scenarios were simulated for both PIC and 13D (Table 1).

Cumulative emissions were reported as Emission Ratio (ER = fumigant volatilized/total fumigant applied). The ER for each model run was reported for 9.25 days, 12.25 days and 15.25

1001 | Street • P.O. Box 4015 • Sacramento, California 95812-4015 • www.cdpr.ca.gov

days. The 9.25 day output time corresponds to tarpcut, while 12.25 day represents emissions that would be expected from a typical field study lasting 3 days beyond tarp-cut. The 15.25 day reporting time was chosen to ensure that simulated volatilization was essentially complete.



Figure 1. Modeling scenario for strip applications. Thick dark line is the TIF tarp; "boxes" at 46 cm depth (18 inch) represent assumed initial concentration condition for simulation. The modeling domain represents the "half-width" of a single tarp plus untarped application pass.

Table 1. 13D and PIC application scenarios for simulations.

	DEPTH OF		
TYPE APPLICATION	APPLIC (IN)	Tarp	
BROADCAST	18"	none	
BROADCAST	18"	FULL	
strip, 7 shanks	18"	STRIP	

Initial Soil-Water Contents

Each scenario was simulated using 3 initial soil water content conditions: "wet", "moist", and "label minimum" (Table 2). The "moist" conditions are the initial soil water contents measured in Lost Hills field 1, while the "wet" condition are those measured in Lost Hills field 3 (wettest of the Lost Hills fields). The "label minimum" water contents were calculated from measured field 1 Lost Hills retention data, and correspond to the minimum allowable pre-application soil moisture allowed by fumigant labels (50% available water capacity, AWC). The total (100%) AWC is the amount of water held between field capacity (FC) and permanent wilting point (PWP). For example, if a soil has FC=0.25 and PWP = 0.05, and the volumetric water content is 0.15, then the AWC at that water content = (water content - PWP)/(FC – PWP) = 0.5 = 50%.

Table 2. Initial water contents used for each scenario. The fumigant injection was at the 46 cm depth (18").

expressed as Available Water Content

	label minimum	<u>moist</u>	wet
depth (cm)	field 1	field 1	field 3
0-20	0.50	0.509	0.795
20-40	0.50	0.712	0.879
40-60	0.50	0.719	1.007

expressed as Volumetric Water Content

	label minimum	<u>moist</u>	wet
depth (cm)	field 1	field 1	field 3
0-20	0.177	0.178	0.213
20-40	0.190	0.216	0.262
40-60	0.214	0.241	0.299

Temperature, tarp and fumigant properties

The HYDRUS default sine wave soil surface temperature boundary condition was used for the bare ground (untarped) portion of the modeling domains, with mean temperature and diurnal amplitude estimated from daily max/min temperature data over the June 4 – June 21, 2011 Lost Hills study period. All other input data, including under tarp soil surface temperatures, tarp properties, fumigant physicochemical properties, and soil properties were those used in the Lost Hills simulations. Those data are available in Appendix 1 of Spurlock et al., 2013a.

RESULTS

13D

The first three 13D simulation results (Table 3) are for a bare ground broadcast application, and allow comparison to field data for VOC fumigant application method 1206 (deep untarped broadcast application, Barry et al., 2007). The method 1206 ER is 26% for 13D, while the simulations here yielded 0.11 < ER < 0.24. Given the inherent uncertainty in field data and variability in soil conditions, the method 1206 fluxes and simulated fluxes here agree relatively well. Simulations 5 and 6 are fully tarped TIF broadcast applications based on soil properties and initial water content measured in Lost Hills fields 1 (moist) and 3 (wet). Tarpcut was simulated at 9.25 days here, and the moist scenario ER was 0.027 at that time. Lost Hills field 1 ER at 9.25 days was 0.076, the difference attributable to the deeper injection as compared to Lost Hills (18" versus 12"), and the much wetter soil-water content at that depth in the simulation here.

Cumulative emission varied across the surface of the strip application scenario, with highest volatilization occurring at a narrow strip of bare soil next to the edge of the tarp (Figure 2). The contribution of bare soil areas to cumulative flux decreased rapidly with distance from the tarp, dropping to near zero at the right hand side of the modeling domain. Consequently, applications with a larger proportion of bare ground are predicted to yield essentially identical ERs providing the same application depth, shank and tarp configurations are used.

Table 3. Simulated 13D Emission Ratios

13D

	Initial		Emi	ssion Ratios	
Type Application	Soil Moisture	Tarp	at 9.25d tarpcut	12.25d	15.25d
BROADCAST	label minimum	none	0.211	0.228	0.235
BROADCAST	moist	none	0.173	0.190	0.197
BROADCAST	wet	none	0.084	0.101	0.109
BROADCAST	label minimum	FULL	0.031	0.032	0.033
BROADCAST	moist	FULL	0.025	0.027	0.027
BROADCAST	wet	FULL	0.013	0.022	0.023
strip 7 shank	label minimum	STRIP	0.052	0.064	0.067
strip 7 shank	moist	STRIP	0.042	0.054	0.056
strip 7 shank	wet	STRIP	0.017	0.027	0.029

PIC

Initial			Emission Ratios		
Type Application	Soil Moisture	Tarp	at 9.25d tarpcut	12.25d	15.25d
BROADCAST	label minimum	none	0.179	0.186	0.189
BROADCAST	moist	none	0.147	0.154	0.157
BROADCAST	wet	none	0.073	0.081	0.084
BROADCAST	label minimum	FULL	0.017	0.017	0.017
BROADCAST	moist	FULL	0.014	0.014	0.014
BROADCAST	wet	FULL	0.007	0.007	0.007
strip 7 shank	label minimum	STRIP	0.035	0.038	0.039
strip 7 shank	moist	STRIP	0.028	0.032	0.032
strip 7 shank	wet	STRIP	0.013	0.016	0.016

Although the 13D strip ERs varied with initial soil moisture content, the relative differences in ER between the strip and fully tarped broadcast applications were similar for the three soil moisture regimes simulated. The ratio of strip to tarped broadcast ER ranged from 1.24 (wet) to 2.1 (dry) (Table 3).



Figure 2. Simulated *specific* cumulative flux (cumulative mass per unit area, ug m⁻²) for a theoretical 100 kg ha⁻¹ 13D application using Lost Hills field 1 ("moist") soils data. The center of the application corresponds to the left hand side of the domain in Figure 1. The "whole-field" (tarped + untarped area) mean *specific* cumulative flux across the entire domain was 0.57 g m⁻².

PIC

Similar to the 13D simulations, the first 3 PIC simulation in Table 3 are for a bare ground broadcast application, to allow comparison to field data for VOC fumigant application method 1206 (deep untarped broadcast application, Barry et al., 2007). However, here the agreement between these simulations and the method 1206 field-based PIC data is relatively poor; the method 1208 ER of 0.64 is based on an Arizona study (Beard et al., 1996). For the simulated results here, 0.08 < ER < 0.19 (Table 3). The reason for the discrepancy is unclear, and may be related to differences in soil properties or initial soil-water contents, error in estimating field-estimated flux, or some combination. However, here we are determining relative ER differences between 2 application methods, so assume the model accurately reflects those differences.

Simulations 5 and 6 are fully tarped TIF broadcast applications based on soil properties and initial water content measured in Lost Hills fields 1 (moist) and 3 (wet). Tarpcut was simulated at 9.25 days here, and the moist scenario ER was 0.025 at that time. Lost Hills field 1 ER at 9.25 days was 0.038, the difference attributable to the deeper depth simulated here (18") versus depth of application in Lost Hills (12").

Cumulative emission varied across the surface of the strip application scenario, with highest volatilization occurring at a narrow strip of bare soil next to the edge of the tarp (Figure 3). The contribution of bare soil areas to cumulative flux decreased rapidly with distance from the tarp, dropping to near zero at the right hand side of the modeling domain. Consequently, applications with a larger proportion of bare ground should yield essentially identical ERs providing the same application depth, shank and tarp configurations are used.



Figure 3. Simulated *specific* cumulative flux (cumulative mass per unit area, ug m⁻²) for a theoretical 100 kg ha⁻¹ PIC application using Lost Hills field 1 ("moist") soils data. The center of the application corresponds to the left hand side of the domain in Figure 1. The "whole-field" (tarped + untarped area) mean *specific* cumulative flux across the entire domain was 0.32 g m⁻².

Although the PIC strip ERs varied with initial soil moisture content, the relative difference in ER between the strip and fully tarped broadcast applications were similar for the three soil moisture regimes simulated. The ratio of strip to fully tarped broadcast ER ranged from 2.18 to 2.25 (Table 3).

CONCLUSION

HYDRUS 2D/3D was used to evaluate the relative effect on ER of strip TIF applications as compared to bare ground and fully TIF tarped broadcast applications for both 13D and PIC. The simulations assume the fine sandy loam soil is well-tilled with no clods, properties identical to field soils in the recent Lost Hills study (Spurlock et al., 2013b) and initial soil moisture consistent with label requirements. Deviations from these conditions would likely yield different results. Under these conditions, in most cases the cumulative flux expressed as emission ratio for the 18" deep TIF strip applications were approximately twice those from the fully tarped broadcast. However, both strip and fully TIF tarped simulations yielded much lower emissions

than in the corresponding bare ground case. For both fumigants, fumigant flux falls off rapidly with distance from the tarp edge. Thus, the results are generally applicable; other strip scenarios with larger bare ground widths would yield essentially identical results assuming the shank spacing, TIF tarp widths and application depth as in Figure 1.

REFERENCES

- Barry, T., F. Spurlock and R. Segawa. September 29, 2007, memorandum to J. Sanders: Pesticide Volatile Organic Compound Emission Adjustments For Field Conditions And Estimated Volatile Organic Compound Reductions–Revised Estimates. On-line: <u>http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/1955_sanders.pdf</u>
- Beard, K.K., P.G. Murphy, D.D. Fontaine, J.T. Weinberg. 1996. Monitoring of potential worker exposure, field flux and off-site air concentration during chloropicrin field application. HEH 160. Chloropicrin Manufacturers Task Force. DPR Registration data. Volume199-072.
- Spurlock, F., B. Johnson, and A. Tuli. 2013a, memorandum to Randy Segawa: HYDRUS Simulation of Chloropicrin and 1,3-Dichloropropene Transport and Volatilization in the Lost Hills Fumigation Trials. Online: <u>http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/2420-</u> segawa final.pdf
- Spurlock, F., B. Johnson, A. Tuli, S. Gao, J. Tao, F. Sartori, R. Qin, D. Sullivan, M. Stanghellini and H. Ajwa. 2013b. Simulation of Fumigant Transport and Volatilization from Tarped Broadcast Applications. Vadose Zone Journal. doi:10.2136/vzj2013.03.0056.
- Tuli, A., 2011. Modeling and Monitoring Field Emissions of Fumigants Under Totally Impermeable Films (TIF). Environmental Monitoring Protocol for Study 273. On-line: <u>http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study273protocol.pdf</u>