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SUBJECT: ANALYSIS OF HIGH BARRIER TARPAULIN CIS-1,3-DICHLOROPROPENE MASS TRANSFER COEFFICIENT DATA MEASURED UNDER HIGH RELATIVE HUMIDITY CONDITIONS

INTRODUCTION

"Totally impermeable films" (TIF) display much lower fumigant permeabilities than conventional tarping materials such as polyethylene (Papiernik et al., 2010). The United States Environmental Protection Agency (U.S. EPA) allows buffer zone "credits" (reductions) if applicators use tarps that are highly impermeable to soil fumigants with their applications. The U.S. EPA also identifies low permeability tarps that are eligible for buffer zone credits based on laboratory mass transfer coefficient (MTC) data (http://www.epa.gov/soil-fumigants/tarps). However, these MTC data, a measure of tarp permeability, should be collected under high humidity conditions because the fumigant labels require minimum soil moisture levels at the time of application to reduce fumigant losses to the atmosphere. To achieve the minimum soil moisture levels required, the pre-application area is irrigated, and these conditions result in high under-tarp relative humidity (RH). For example, Spurlock et al. (2013) measured the diurnal fluctuations in under-tarp RHs, which generally ranged between 70 and 95 percent in a broadcast TIF soil fumigation study in Lost Hills, California. Qian et al. (2011) showed that TIF MTCs vary substantially with RH. The RH effect varies but increases of 2 to 3 orders of magnitude in MTC have been measured at 90% RH relative to ambient RH for many TIF tarps. Thus, DPR requires MTC data to be measured under high humidity (RH ≥ 90%) conditions as one of the criteria for inclusion on a California-specific approved tarp list. Tarps on this list are eligible for a 60 percent buffer zone reduction credit in field fumigations (DPR, 2015). Spurlock (2015) made such an analysis for chloropicrin and showed that high barrier tarps should have a MTC of less than 0.0.26 cm/h to be eligible on the list. While this memo summarizes TIF MTC data submitted by tarp manufacturers to DPR as of May 2022, with an emphasis on cis-1,3-dichloropropene (1,3-D) MTCs, it also proposes overall MTC criteria for tarpaulins to be considered TIF for 1,3-D field fumigation. In this memorandum, two approaches are used to determine the MTC criteria; one follows the same approach used by Spurlock (2015) hereafter called “statistical method”, and the other one uses the ratio between laboratory measured and field estimated MTC values, hereafter called “linear ratio method”.

STATISTICAL METHOD

MTC DATA

We evaluated 1,3-D MTC data submitted by different manufacturers for 17 TIF tarps. All submitted MTC data were obtained using permeability chambers as described in American Society for Testing and Materials (ASTM) method E2945-14 (ASTM, 2014). This test method uses a sealed apparatus consisting of two chambers with known volumes separated by the test-tarp membrane. The test fumigant in the vapor phase is added to the chamber on one side of the tarp and the apparatus is incubated at constant temperature under high RH conditions during which the fumigant diffuses through the test tarp. This test method requires the determination of the relative fumigant concentrations on both sides of the membrane (source and receiving chambers) at several time points during the incubation. Concentrations are monitored until equilibrium is reached or the determination of some other practical end time (e.g., very low film permeability may lead to timeframes too long to anticipate equilibrium time). The MTC is determined by fitting the concentration versus time data in both chambers to an analytical model given in ASTM method E2945-14 (ASTM, 2014). Triplicate data were submitted for each fumigant-tarp combination.

Table 1. Tarp names and their manufacturers used in this evaluation.

Manufacturer	**Tarp**
Next Generation Films Inc.	Next Generation TIF DN MULCH, ≥ 1.0 mil
Filmtech Corp.	Filmtech Grozone MAX TIF, 1.25 mil
Ginegar Plastic Products Ltd.	Ginegar Ozgard T Plus, ≥ 1.0 mil, TIF
Coveris-Guardian AgroPlastics	Guardian TIF, ≥ 1.1 mil
Imaflex USA Inc.	Imaflex USA Can-Block Clear v-TIF XSB, 0.9 mil
Plainnova S. de RL de CV	PLAINNOVA MIF MAXIMUM IMPERMEABLE FILM ®
Plainnova S. de RL de CV	PLAINNOVA UBF ULTRA100 ≥ 1.0 mil
AEP Industries Inc.	AEP Sunfilm UltraShield, EVOH barrier, 1.0 mil
TRM Manufacturing	TRM Manufacturing Weather-all Power Film HB 125, ≥ 1.25 mil
Solplast S.A.	REYTIF ≥ 20 micron (≥ 0.8 mil); SOLTIF ≥ 20 micron (≥ 0.8 mil); SOTRAFILM TIF ≥ 20 micron (≥ 0.8 mil)
Berry Plastics	Berry Plastics TOTAL BLOCKADE TIF, 1.25 mil
EcoPoly Solutions Inc.	EcoPoly Gas Stop XXX ≥ 1.0 mil
Polyplex USA	Polyplex BBTIFF01FI TIF ≥1.1 mil
PolySur SA de CV	PolySur TIF ≥1.4 mil (≥35 micron)
ICUSA agroplásticos	AgroSIF 015 Super Impermeable Film, EVOH barrier, 1.0 mil
Raven Industries	Raven TIF VaporSafe, ≥ 1 mil

Imaflex	Imaflex USA Can-Block Clear v-TIF XSB, 0.8 mil

MEAN 1,3-D MTCs

Tarp permeability can drastically change under field conditions due to high RH conditions under the tarp because of pre-application irrigation. Spurlock (2015) clearly showed that in nearly all cases, the low humidity MTC measurements were much lower than those measured under high humidity conditions. Spurlock et al. (2013) measured under-tarp RH and demonstrated that the RH level reaches up to 95% for several days after application. Therefore, DPR considers only high humidity average MTC measurements as representative of more realistic field conditions. We evaluated the high humidity 1,3-D mean MTCs for the 17 tarps, which ranged from <0.0001 to 0.253 cm/h with a median of 0.0153 cm/h (Table 2). Detailed data for all replicates used in this document are given in Appendix 1.

Table 2. Mean standard deviation and CV for submitted 1,3-D MTC data.

Tarp	Mean MTC	SD	CV	Replicates
	cm/h	cm/h	%	-
Next Generation TIF DN MULCH, ≥ 1.0 mil	0.0150	0.0011	7.27	3
Filmtech Grozone MAX TIF, 1.25 mil	0.0199	0.0020	10.02	3
Ginegar Ozgard T Plus, ≥ 1.0 mil, TIF	0.0412	0.0034	8.29	3
Guardian TIF, ≥ 1.1 mil	0.0157	0.0038	24.01	3
Imaflex USA Can-Block Clear v-TIF XSB, 0.9 mil	0.0476	0.0017	3.58	3
Imaflex USA Can-Block Clear v-TIF XSB, 0.8 mil	0.2534	0.0821	32.40	3
PLAINNOVA MIF MAXIMUM IMPERMEABLE FILM ®	0.0184	0.0044	23.84	3
PLAINNOVA UBF ULTRA100 ≥ 1.0 mil	0.0135	0.0029	21.81	5
AEP Sunfilm UltraShield, EVOH barrier, 1.0 mil	0.0047	0.0015	32.31	3
TRM Manufacturing Weather-all Power Film HB 125, ≥ 1.25 mil	0.0340	0.0050	14.76	3
Solplast S.A. REYTIF ≥ 20 micron; SOLTIF ≥ 20 micron ; SOTRAFILM TIF ≥ 20 micron (≥ 0.8 mil)	0.0080	0.0026	32.76	4
Berry Plastics TOTAL BLOCKADE TIF, 1.25 mil	0.0226	0.0165	73.19	3
EcoPoly Gas Stop XXX ≥ 1.0 mil	0.0080	0.0014	17.80	3
Polyplex BBTIFF01FI TIF ≥1.1 mil	0.0084	0.0011	13.20	5
PolySur TIF ≥1.4 mil (≥35 micron)	0.0132	0.0053	40.28	4
AgroSIF 015 Super Impermeable Film, EVOH barrier, 1.0 mil	0.0150	0.0093	62.10	3
Raven TIF VaporSafe, ≥ 1 mil	<0.0001*	-	-	3

* Three Raven replicates were below the minimum quantifiable MTC of 0.0001.	N =	57

To evaluate whether there were any outliers in the submitted MTC data, a graphical analysis of means was used as demonstrated in Spurlock (2015) for identifying any data groups that significantly differed from the overall grand mean across all groups. Figure 2 depicts the results of the analysis of the means (ANOM) approach. In Figure 1, the Imaflex USA Can-Block v-TIF 0.8 mil is approximately 8 times greater than the grand mean MTC across all tarps and more than 5 times greater than the next highest MTC of the Imaflex USA Can-Block v-TIF 0.9 mil. This result was not surprising since Spurlock (2015) found a similar tendency: the Imaflex tarp (0.8 mil) for chloropicrin MTC was also an outlier. Moreover, ANOM analysis indicated that 8 out of 16 mean MTCs of the evaluated tarps were below the lower control limit (Figure 1). In those cases, DPR accepts that these tarps have very low permeability even though there is uncertainty in determining the exact low values.

The mean 1,3-D MTC for all 16 tarps was 0.0170 cm/h with a standard deviation of 0.0131 cm/h. We excluded the Imaflex USA Can-Block v-TIF 0.8 mil from statistical analysis; therefore, we used a total of 54 individual MTC values. The mean 1,3-D for all 16 tarps was different than the overall grand mean across all groups in the ANOM. The reason is because the number of individual values accounted in the mean analysis were different. The mean value was calculated from 54 individual MTC values from all 16 tarps (excluding Imaflex 0.8 mil tarp) while the overall grand mean in the ANOM was calculated from same count of repetitive values (3 in this case and N = 17x3 = 51) to compare the means of 17 tarps (including Imaflex 0.8 mil tarp). Table 3 shows the summary statistics of 16 tarps excluding Imaflex 0.8 mil tarp. Most of the MTC data was the result of 3 replicates but some of the tarp data had 4 or 5 replicates. All these replicates were included in Table 3 as summary statistics to better describe the statistical properties of the MTCs. The 95th percentile of the 54 individual measurements was 0.0466 cm/h.

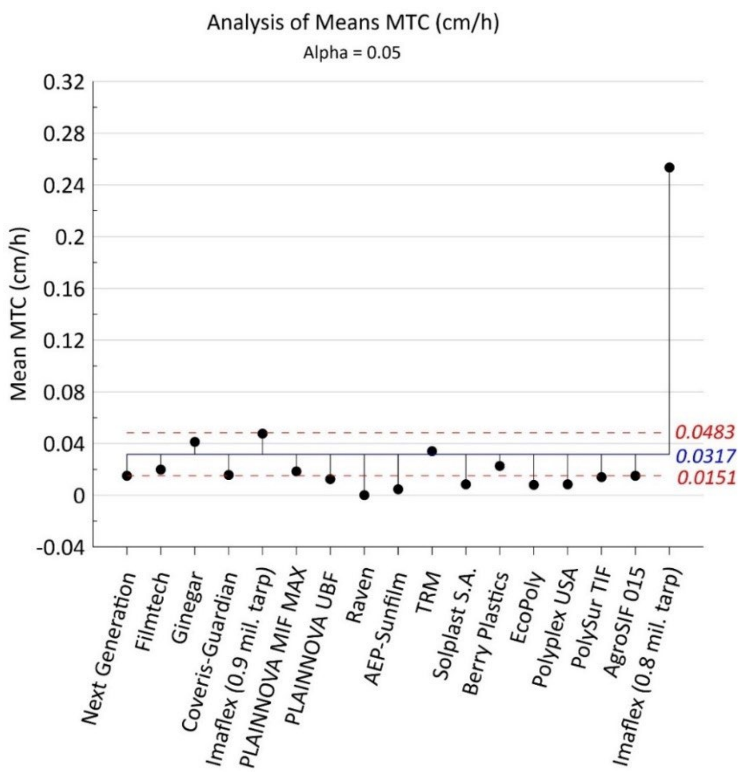

Figure 1. ANOM chart for high humidity 1,3-D MTCs of 17 tarps. The red horizontal dashed lines are decision limits and are the (1-alpha) critical values. The blue horizontal center line at 0.0317 is the grand mean of all individual MTCs.

Table 3. Summary statistics for all 1,3-D MTC replicate measurements on 16 high RH tarps (N=54).

Statistic	High RH MTC (cm/h)
Minimum	0
Average	0.0170
Median	0.0138
95th percentile	0.0466
Maximum	0.0496
Standard Deviation	0.0131

VARIABILITY

Coefficients of variation (CV = standard deviation / mean) were generally highest for the lowest permeability tarps except for the Raven TIF tarp, which has basically no measurable MTC (Figure 2). As Spurlock (2015) pointed out, this is partially attributable to the greater variability in quantifying small changes in concentration associated with very low MTCs. Thus, there is uncertainty in estimating those low MTCs when concentration changes are small. An additional factor is the arithmetic form of CVs, where very low means in the denominator tend to yield high CVs. Figure 2 suggests that most MTC CVs are below 40%, except for the example of Berry Plastic Total Blockade TIF (CV = 73%, mean MTC = 0.0226 cm/h). Therefore, MTC CVs below 40% should generally be obtainable for TIF MTC data for most fumigants. Even in cases where the CV is high, DPR may reasonably conclude, following a review of available data, that a tarp has very low permeability even though there is uncertainty in just how “low” that permeability (i.e., MTC) is.

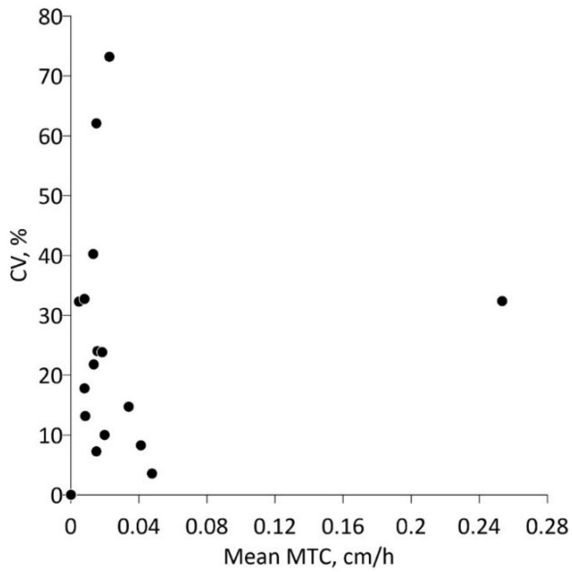

Figure 2. CV vs mean MTC for reported triplicate MTC determinations. Data for 1,3 - dichloropropene on 17 tarps are shown.

LINEAR RATIO METHOD

In the previous section, we followed the procedure previously used to determine the threshold MTC value for chloropicrin, calculated as the 95th percentile of the 54 individual measurements of MTCs as 0.0466 cm/h, and we used a recommended threshold MTC value for TIF tarp eligibility. Spurlock et. al. (2013) conducted a field study to estimate the emission of chloropicrin and 1,3-D from a TIF-tarped application site. The estimated field-scale MTC value for chloropicrin and 1,3-D was 0.12 cm/h and 0.21 cm/h, respectively. As an alternative approach and to account for field-scale MTC values, we tried a simple ratio method to determine the threshold MTC value for 1,3-D. This method uses the ratio of field-scale MTC values of chloropicrin and 1,3-D and laboratory-tested chloropicrin threshold MTC value of 0.026 cm/h calculated by Spurlock (2015). Following the simple ratio method, we can find the laboratory-tested MTC value for 1,3-D under high RH as follows:

Lab tested MTC threshold for 1,3-D = $\frac{0.026\ cm/h \times 0.21\ cm/h}{0.12\ cm/h} = 0.0455\ cm/h$

The MTC threshold value of 0.0455 cm/h, determined in this approach, is very close to the calculated 95th percentile MTC threshold value of 0.0466 cm/h.

CONCLUSIONS

- DPR only accepts MTCs of barrier tarps determined under high RH conditions due to their being more representative of field conditions and their much higher value than MTCs determined under low RH conditions.
- ANOM indicated that the Imaflex USA Can-Block v-TIF (0.8 mil. tarp) has a very high mean MTC for 1,3-D, which was significantly greater than the overall mean obtained from all individual MTC values. This result was similar to the case observed with chloropicrin where the same tarp had a much greater MTC value than other barrier tarps. Therefore, that tarp was determined to be unacceptable for inclusion in the list of TIF-tarpaulins approved by DPR.
- After overall statistical analysis, we found that the mean high RH 1,3-D MTC of 16 tarps was 0.0170 cm/h with a standard deviation of 0.0131cm/h. The 95th percentile of 54 individual MTC values was 0.0466 cm/h.
- Using an alternative simple ratio method, the MTC threshold value of 1,3-D was calculated to be 0.0455 cm/h, which is very close to MTC threshold value of 0.0466 cm/h calculated with the 95th percentile method.
- Based on the MTC values estimated in this analysis, the recommended MTC threshold value for 1,3-D is 0.046 cm/h, resulting in the disqualification of Imaflex USA Can-Block v-TIF (0.9 mil. tarp) as TIF tarp due to higher MTC value of 0.0476 cm/h.

REFERENCES

ASTM. 2014. Method E2945-14: Standard Test Method for Film Permeability Determination Using Static Permeability Cells. DOI: 10.1520/E2945-14

DPR. 2015. April 8, 2015, letter from C.M. Andrews, DPR Associate Director, to Agricultural Film Manufacturers RE: TARPAULINS USED FOR CHLOROPICRIN PERMIT CONDITIONS.

Qian, Y., Kamel, A., Stafford, C., Nguyen, T., Chism, W.J., Dawson, J., and C. W. Smith. 2011. Evaluation of the permeability of agricultural films to various fumigants. Environ. Sci. Technol. 45:9711–9718.

Paperniek, S.K., S.R. Yates, and D. O. Chelemi. 2010. A Standardized Approach for Estimating the Permeability of Plastic Films to Soil Fumigants under Various Field and Environmental Conditions. J. Env. Qual. doi:10.2134/jeq2010.0118.

Spurlock, F., B. Johnson, A. Tuli, S. Gao, J. Tao, F. Sartori, R. Qin, D. Sullivan, M. Stanghellini and H. Ajwa. 2013. Simulation of Fumigant Transport and Volatilization from Tarped Broadcast Applications. Vadose Zone Journal. doi:10.2136/vzj2013.03.0056.

Spurlock, F. 2015. ANALYSIS OF HIGH BARRIER TARPAULIN CHLOROPICRIN MASS TRANSFER DATA MEASURED UNDER HIGH RELATIVE HUMIDITY CONDITIONS. Memorandum to Pamela Wofford. Department of Pesticide Regulation, Sacramento.

APPENDIX 1. 1,3-DICHLOROPROPENE HIGH RELATIVE HUMIDITY MTC DATA – ALL REPLICATES

Tarpaulin Name	MTC Replicates (cm/h)					MTC Average	Std. Deviation	CV %
	# 1	# 2	# 3	# 4	# 5			
AEP Sunfilm UltraShield, EVOH barrier, 1.0 mil	0.0046	0.0032	0.0063			0.0047	0.0015	32.3
AgroSIF 015 Super Impermeable Film, EVOH barrier	0.0092	0.0257	0.0100			0.0150	0.0093	62.1
Berry Plastics TOTAL BLOCKADE TIF, 1.25 mil	0.0131	0.0417	0.0130			0.0226	0.0165	73.2
Coveris-Guardian TIF, ≥ 1.1 mil	0.0198	0.0147	0.0125			0.0157	0.0038	24.0
EcoPoly Gas Stop XXX ≥ 1.0 mil	0.0092	0.0084	0.0064			0.0080	0.0014	17.8
Filmtech Grozone MAX TIF, 1.25 mil	0.0204	0.0216	0.0177			0.0199	0.0020	10.0
Ginegar Ozgard T Plus, ≥ 1.0 mil, TIF	0.0373	0.0438	0.0425			0.0412	0.0034	8.3
Imaflex USA Can-Block Clear v-TIF XSB, 0.8 mil	0.3480	0.2125	0.1998			0.2534	0.0821	32.4
Imaflex USA Can-Block Clear v-TIF XSB, 0.9 mil	0.0496	0.0465	0.0468			0.0476	0.0017	3.6
Next Generation TIF DN MULCH, ≥ 1.0 mil	0.0161	0.0139	0.0150			0.0150	0.0011	7.3
PLAINNOVA MAXIMUM IMPERMEABLE FILM	0.0182	0.0141	0.0228			0.0184	0.0044	23.8
PLAINNOVA UBF ULTRA100 ≥ 1.0 mil	0.0085	0.0136	0.0153	0.0142	0.0158	0.0135	0.0029	21.8
Polyplex BBTIFF01FI TIF ≥1.1 mil	0.0069	0.0094	0.0089	0.0079	0.0070	0.0080	0.0011	13.8
PolySur TIF ≥1.4 mil (≥35 micron)	0.0199	0.0146	0.0077	0.0104		0.0132	0.0053	40.3
Raven TIF VaporSafe, ≥ 1 mil	0.0000	0.0000	0.0000			0.0000	0.0000	0.0
SOTRAFILM TIF ≥ 20 micron (≥ 0.8 mil)	0.0112	0.0089	0.0053	0.0065		0.0080	0.0026	32.8
TRM Manufacturing Weather-all Power Film HB 125	0.0294	0.0393	0.0334			0.0340	0.0050	14.8