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SUBJECT: ANALYSIS OF HIGH BARRIER TARPAULIN CHLOROPICRIN MASS TRANSFER DATA MEASURED UNDER HIGH RELATIVE HUMIDITY CONDITIONS

INTRODUCTION

"Totally impermeable films" (TIF) display much lower fumigant permeabilities than do conventional tarping materials such as polyethylene (PE) (Papiernik et al., 2010). The United States Environmental Protection Agency (U.S. EPA) allows buffer zone "credits" (reductions) for TIF soil fumigations as compared to bare ground- or PE-type applications. The U.S. EPA identifies low permeability tarps that are eligible for buffer zone credits based on laboratory mass transfer coefficient (MTC) data (http://www2.epa.gov/soil-fumigants/tarps). However, these MTC data, a measure of tarp permeability, are typically collected under ambient humidity conditions.

Fumigant labels require minimum soil moisture levels at the time of application to reduce fumigant losses to the atmosphere; these are usually achieved by pre-application irrigation. These conditions promote high under-tarp relative humidity (RH). For example, diurnal fluctuations in under-tarp RHs generally ranged between 70 and 95 percent in a recent California broadcast TIF soil fumigation (Spurlock et al., 2013). TIF MTCs vary substantially with RH. The effect varies, but increases of 2 to 3 orders of magnitude in MTC have been measured at 90 percent RH relative to ambient RH for many TIF tarps (Qian et al., 2011). Due to concern over the impact of humidity on TIF tarp permeability, DPR has requested TIF tarp manufacturers submit MTC data measured under high humidity conditions (≥ 90%; DPR, 2015). DPR intends to use these high humidity MTC data to develop a California-specific approved high barrier tarp list eligible for a 60 percent buffer zone reduction credit in chloropicrin field fumigations. This memo summarizes TIF MTC data submitted to DPR as of November 2015, with an emphasis on chloropicrin MTCs.

MTC DATA

MTC data were submitted for 10 TIF tarps. The MTC data were obtained using permeability cells as described in ASTM method E2945 (ASTM, 2014). Generally, the permeability cell is a sealed cylinder consisting of two chambers between which the test plastic is placed. Fumigants are introduced into the chamber on one side of the film (source chamber), and fumigant

concentrations in both sides of the tarp (source and receiving chambers) are monitored over time. The MTC is determined by fitting the concentration versus time data in both chambers to an analytical model (ASTM, 2014). Triplicate data were submitted for each fumigant-tarp combination. While DPR's immediate interest was in chloropicrin, data were submitted for several other fumigants for each tarp.

VARIABILITY

Coefficients of variation (CV= standard deviation/mean) were generally highest for the lowest permeability tarps (Figure 1). This is partially attributable to greater variability in quantifying small changes in concentration associated with very low MTCs, and 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 1 suggests that, for MTCs greater than 0.02 cm/h, CVs of 30% or below should generally be obtainable for TIF MTC data with most fumigants. For very low mean MTCs (e.g. <<0.02 cm/h based on these data), high variability may be relatively unimportant for DPR's purposes. In those cases DPR may reasonably conclude the tarp has very low permeability even though there is uncertainty in just how "low" that permeability (i.e. MTC) is.

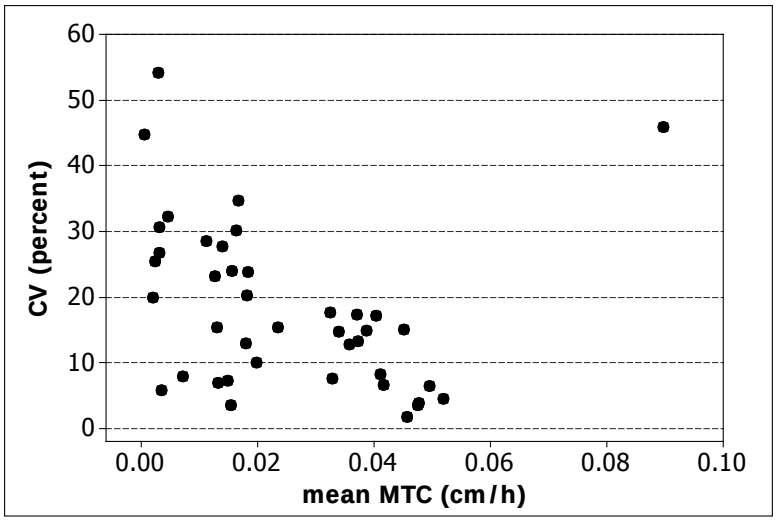

Figure 1. CV vs mean MTC for reported triplicate MTC determinations. Data for 1,3-dichloropropene, dimethyl disulfide, methyl bromide, chloropicrin, and methyl isothiocyanate on 10 tarps are shown.

PERIOD-WISE RECOVERIES

An experimental difficulty that is occasionally observed with the static cell permeability measurement procedure is low fumigant recovery relative to initial fumigant addition at one or more sampling times (ASTM, 2014). Causes may include fumigant degradation, static cell

leakage or fumigant sorption to the tarp. The ASTM method provides general guidance on recoveries, stating when percent recovery "*remains above 60 % for all sample times and all replicates, the concentration measurements can be considered acceptable. Otherwise, it will be necessary to determine if low recovery is due to leakage or sorption. If literature or experimental information is available that rules out sorption as a likely cause of low recovery, the concentrations measurements should be considered questionable*." For the chloropicrin permeability measurements on the high barrier EVOH resin tarps evaluated here, no major problems with chloropicrin sorption, degradation or leakage were evident (Figure 2). Across all tarps, there was a slight decrease in mean recovery after 7 days, but mass recoveries were generally greater than 70% and less than 130% at all sampling intervals.

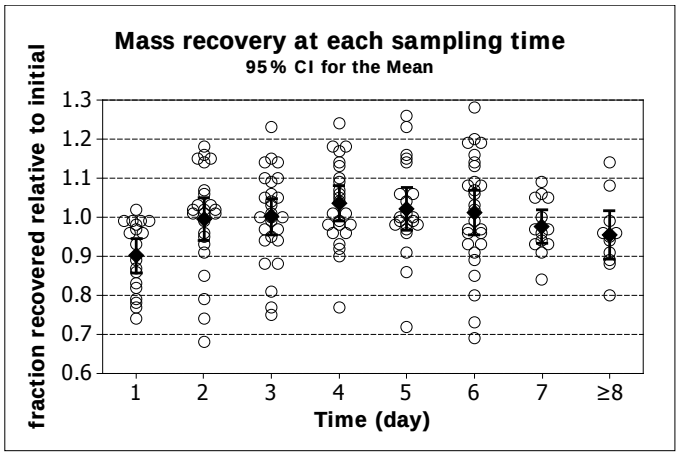

Figure 2. Chloropicrin mass recovery at each sampling. Data for all replicates; recovery expressed as a fraction of initial chloropicrin added.

MEAN CHLOROPICRIN MTCs

In nearly all cases, the low humidity MTC measurements (not shown) were much lower than those measured under high humidity conditions. Nearly half of the low humidity measurements were < 0.0001 cm/h and are no longer considered here. The high humidity chloropicrin mean MTCs for the 10 tarps ranged from <0.0001 to 0.0898 cm/h with a median of 0.0035 cm/h (Table 1). Detail data for all replicates are shown in Appendix 1. Qian et al. (2011) tested 10 TIF tarps under high humidity conditions, obtaining mean chloropicrin MTCs ranging from 0.0001 to 0.963 cm/h, with a median of 0.0034 cm/h. Gao et al. (2013) reported a mean chloropicrin MTC of 0.0192 cm/h (0.0136, 0.0248; 95% confidence interval) for used samples of a Raven VaporSafe TIF tarp. The tarp had been deployed in a field study where undertarp RH of up to 95% had been measured for several days (Spurlock et al., 2013). The magnitude of most of the

mean chloropicrin MTCs reported to DPR are generally consistent with the data of Qian et al. (2011) and Gao et al. (2013).

Table 1. Mean, standard deviation and CV for submitted chloropicrin MTC data

Tarp	mean MTC (cm/h)	sd	CV (percent)
AEP-Sunfilm™ Ultrashield	0.0007	0.0003	44.8
Coveris-Guardian TIF	0.0035	0.0002	5.7
Filmtech Gro+Zone MAX	0.0032	0.0009	26.7
Ginegar Ozgard T Plus	0.0130	0.0020	15.4
Imaflex USA Can-Block v-TIF (0.8 mil. tarp)	0.0898	0.0412	45.9
Imaflex USA Can-Block v-TIF (0.9 mil. tarp)	0.0236	0.0036	15.3
Next Generation Films TIF DN MULCH	0.0025	0.0006	25.5
PLAINNOVA MIF MAXIMUM IMPERMEABLE FILM	0.0031	0.0017	54.2
Raven TIF VaporSafe™	<0.0001*	-----	-----
TRM Manufacturing Weather-all Power Film HB 125	0.0164	0.0049	30.0

***** Two of the three Raven replicates were below the minimum quantifiable MTC of 0.0001. The third replicate was 0.0001.

A graphical analysis of means (ANOM) shows an outlier in the group (Figure 3). ANOM is a commonly used quality control procedure to identify which, if any, data groups are statistically different than the overall grand mean across all groups. The high MTC displayed by the Imaflex Can-Block 0.8 mil tarp is a factor of ~ 6 greater than the grand mean MTC across all tarps and nearly 4 times greater than the next highest MTC. In recent field studies, chloropicrin soil-gas concentrations under the Imaflex 0.8 mil tarp declined much more rapidly than those under several other of the TIF tarps (H. Aajwa, personal communication), suggesting higher permeability. Finally, the Imaflex 0.8 mil tarp is the thinnest of the films tested here.

For the remaining 9 tarps (excluding the Imaflex 0.8 mil tarp), the mean chloropicrin MTC was 0.00732 cm/h (± 0.00829 SD). Summary statistics for the 9 tarps are shown in Table 2. By way of comparison, recently measured chloropicrin MTCs for conventional high density polyethylene tarps range from 0.78 to ~4.8 cm/h, with the majority of measurements between 1.5 and 3 cm/h (Papiernik et al., 2010; Qian et al., 2011).

Table 2. Summary statistics for all MTC replicate measurements on 9 high barrier tarps (N=27; excludes Imaflex 0.8 mil tarp data).

Statistic	High RH MTC (cm/h)
minimum	< 0.0001
median	0.00342
95^{th} percentile	0.0257
maximum	0.0273

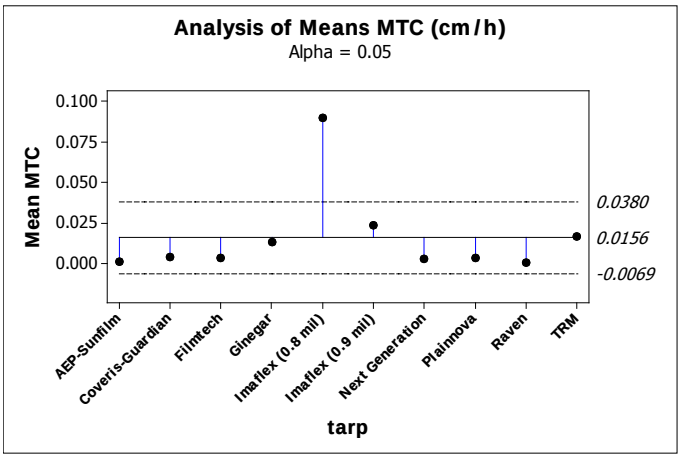

Figure 3. ANOM chart for high humidity chloropicrin MTCs of 10 tarps. The horizontal reference line at 0.0156 is the grand mean. The dashed lines are known as "decision limits", and are the (*1-alpha*) critical values for the ANOM procedure.

CONCLUSION

- Consistent with previous studies, MTCs determined under high humidity conditions were much greater than those determined under low humidity conditions.
- For MTCs greater than about 0.020 cm/h, CVs were less than 0.3. For the very low MTCs, higher CVs were observed but this may be of less practical importance. In those cases DPR may reasonably conclude the tarp has very low permeability even though there is uncertainty in just how "low" that permeability is.
- The Imaflex USA Can-Block v-TIF (0.8 mil. tarp) displayed a mean MTC for chloropicrin that was significantly greater than the overall grand mean, and several times higher than the next highest tarp MTC. That 0.8 mil tarp is the thinnest of all the tarps tested, and field data indicate rapid dissipation of under-tarp chloropicrin indicating higher permeability relative to other high barrier tarps tested.
- The mean high RH chloropicrin MTC for 9 tarps (excluding the Imaflex 0.8 mil tarp) was 0.00732 cm/h (± 0.00829 SD). The 95th percentile of the 27 individual measurements on those tarps was 0.0257 cm/h. For comparison, typical MTCs for conventional high density polyethylene tarps range from approximately 0.78 to 4.8 cm/h.

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Appendix 1 – Chloropicrin MTC data – all replicates

All Chloropicrin high humidity MTC data

Tarp	MTC(cm/h)
AEP-Sunfilm™ Ultrashield	0.00090
AEP-Sunfilm™ Ultrashield	0.00033
AEP-Sunfilm™ Ultrashield	0.00073
Coveris-Guardian TIF	0.00364
Coveris-Guardian TIF	0.00326
Coveris-Guardian TIF	0.00356
Filmtech Gro+Zone MAX	0.00342
Filmtech Gro+Zone MAX	0.00398
Filmtech Gro+Zone MAX	0.00229
Ginegar Ozgard T Plus	0.01534
Ginegar Ozgard T Plus	0.01211
Ginegar Ozgard T Plus	0.01167
Imaflex USA Can-Block v-TIF (0.8 mil. tarp)	0.12915
Imaflex USA Can-Block v-TIF (0.8 mil. tarp)	0.09316
Imaflex USA Can-Block v-TIF (0.8 mil. tarp)	0.04694
Imaflex USA Can-Block v-TIF (0.9 mil. tarp)	0.02734
Imaflex USA Can-Block v-TIF (0.9 mil. tarp)	0.02015
Imaflex USA Can-Block v-TIF (0.9 mil. tarp)	0.02327
Next Generation Films TIF DN MULCH	0.00312
Next Generation Films TIF DN MULCH	0.00240
Next Generation Films TIF DN MULCH	0.00187
PLAINNOVA MIF MAXIMUM IMPERMEABLE FILM	0.00232
PLAINNOVA MIF MAXIMUM IMPERMEABLE FILM	0.00191
PLAINNOVA MIF MAXIMUM IMPERMEABLE FILM	0.00497
Raven TIF VaporSafe™	0.00000
Raven TIF VaporSafe™	0.00001
Raven TIF VaporSafe™	0.00000
TRM Manufacturing Weather-all Power Film HB 125	0.01134
TRM Manufacturing Weather-all Power Film HB 125	0.02118
TRM Manufacturing Weather-all Power Film HB 125	0.01666