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SUBJECT: EVALUATION OF CHLOROPICRIN BUFFER ZONE CREDITS UNDER CALIFORNIA USE CONDITIONS

INTRODUCTION

The United States Environmental Protection Agency (USEPA) recently implemented new safety measures for soil fumigants. The measures are intended to increase protections for agricultural workers and others that are near fields that are fumigated. The changes were phased-in, and included buffer zones around fumigated fields to reduce risks from acute inhalation exposures. Along with other fumigants, chloropicrin specific buffer zone requirements were implemented in “Phase 2” fumigant labels, required as of December 1, 2012 (https://www.epa.gov/sites/production/files/2013-10/documents/sfm-implementation-sched-2012.pdf). Buffer zone distances for specific application scenarios are provided in look-up tables on Phase 2 fumigant labels.

USEPA also provided buffer zone reduction “credits” for users that employ specific application practices such as use of approved high-barrier tarps (e.g. https://www.epa.gov/soil-fumigants/tarps) and post-application irrigations. The rationale for the credits is that application conditions or practices that yield lower fluxes should require smaller minimum buffer zones to provide the same level of bystander protection. Implicit in that logic is that buffer zones vary directly with flux. Johnson (2016) recently evaluated that assumption for California chloropicrin buffer zones, concluding that “In general, it appears that an x% reduction in flux results in *at least* an x% reduction in buffer zones. This implies that a system of buffer zone credits based on a percentage of flux reduction may apply over different application rates or acreages.” Johnson’s analysis therefore supports the underlying rationale for buffer credits.

The ability of high-barrier tarps to reduce fumigant post-application volatilization to the atmosphere relative to polyethylene tarps has been demonstrated (e.g., Spurlock et al., 2013), and is not discussed here. In certain cases post-application irrigations also decrease emissions (Gao et al., 2011). In USEPA phase 2 fumigant labels credits are provided for post-application irrigations and also for other site conditions posited to reduce peak fumigant emissions. These conditions include soil clay content, soil temperature and organic content.

The object of this memorandum is to evaluate the effect of the various buffer zone credit management practices and site conditions on maximum 6 hr chloropicrin flux density (i.e. “flux”) under actual California use conditions. The maximum 6 hr flux is the basis for California’s buffer zones (Barry, 2014). The following label language for the conditions evaluated here are on all phase 2 chloropicrin labels.

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The buffer zone distances for chloropicrin product applications *“may be reduced by the percentages listed below. Credits may be added, but credits cannot exceed 80%.*

- *10% reduction in the buffer zone distance, IF the clay content of the soil in the application block is greater than 27%.*
- *10% reduction in buffer zone distance, IF the soil temperature is measured to be 50°F or less. Record temperature measurements at the application depth or 12 inches, whichever is shallower.*
- *15% reduction in buffer zone distance, IF ¼ to ½ inch of water is applied.*
- *10% reduction in buffer zone distance, IF the organic content of the soil in the application block is > 1% - 2%; a 20% reduction in buffer zone distance, IF the organic content of the soil in the application block is > 2% - 3%; and a 30% reduction in the buffer zone distance, IF the organic content of the soil in the application block is > 3%.”*

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DATA SOURCES AND METHODS

Chloropicrin use data 2013 use data served as the basis for the analyses here. Total chloropicrin applied in that year was 8.2 million pounds, with strawberries accounting for a majority of use (Table 1). Over 90% of chloropicrin was applied in 8 counties in 3 regions: the coastal region, San Joaquin Valley and Siskyou County (Table 2). In the coastal counties and Siskyou County, most applications occurred in mid-summer through early fall, while spring applications dominated in the two San Joaquin Valley counties (Table 3).

NRCS soil data Soil data from the Natural Resource Conservation Service (NRCS) were merged with chloropicrin use data by section (i.e. MTRS; Meridian-Township-Range-Section according to the Public Lands Survey System, http://nationalmap.gov/small_scale/a_plss.html) to obtain texture classification and organic carbon (OC) content for those sections where chloropicrin was applied in the top eight counties in Table 2.

Table 1. 2013 California statewide reported chloropicrin use by application site.

Application Site	Use (lbs)	Fraction of Total
STRAWBERRY (ALL OR UNSPEC)	5976166	0.727
SOIL APPLICATION, PREPLANT-OUTDOOR (SEEDBEDS,ETC.)	755066	0.092
RASPBERRY (ALL OR UNSPEC)	705205	0.086
N-OUTDR GRWN TRNSPLNT/PRPGTV MTRL	250473	0.030
WATERMELONS	95728	0.012
TOMATO	86982	0.011
UNCULTIVATED AGRICULTURAL AREAS (ALL OR UNSPEC)	78006	0.009
PEPPERS (FRUITING VEGETABLE), (BELL,CHILI, ETC.)	61766	0.008
N-OUTDR CONTAINER/FLD GRWN PLANTS	43118	0.005
OTHER	165661	0.020
TOTAL	8218171	1.000

Table 2. 2013 California statewide reported chloropicrin use by county.

COUNTY	Use (lbs)	Fraction of Total
Ventura	2176831	0.26
Monterey	2015006	0.25
Santa Barbara	1275126	0.16
Santa Cruz	662814	0.08
Siskyou	508009	0.06
San Luis Obispo	446953	0.05
Merced	198068	0.02
San Joaquin	185437	0.02
Others	749927	0.09
Total	8218171	1.00

The general procedure for merging the soil and use data was similar to that detailed by Johnson and Spurlock (2009). Briefly, data for 13 soil surveys representing all MTRS in the eight counties were downloaded from the NRCS soil survey website (http://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx). The downloaded data were merged with an existing DPR Oracle California soil database that lists the MUIDs in each MTRS, acreage of each MUID in the MTRS, and total acreage of the MTRS (not all MTRS are 640 acres). An MUID is a “map unit identifier”, a unique code for individual soil type such as Hanford sandy loam. The resulting interim dataset was then merged with the full year of 2013 chloropicrin use by MTRS, and those MTRS with no chloropicrin use were discarded. Each record in the final merged dataset contained the following fields:

- MUID code,
- MUID name (i.e. “soil type”),
- texture,
- MTRS,
- total acreage of the MTRS,
- acreage of the MUID within the MTRS,
- mean depth-averaged soil organic carbon content for each of 3 soil layers in the MUID (0-10 cm, 10 – 30 cm, 30 – 100 cm),
- total chloropicrin applied within the MTRS, and
- MUID apportioned chloropicrin applied.

The MUID apportioned chloropicrin use is pounds of chloropicrin within an MTRS assigned proportionally to the MUID fractional area within that same MTRS. This does not represent exact chloropicrin use on these MUIDs because available use data does not provide that level of specificity.. Thus, strictly speaking, the MUIDs determined in this analysis cannot be described as MUIDs upon which chloropicrin was applied**; instead this apportioning procedure provides estimates of the dominant soil textures (or other MUID-specific soil properties such as soil organic carbon content) of the soils in sections where chloropicrin is used.** Appendix 1 has an example of the final merged soil and use data for one MTRS in Santa Barbara County. The most appropriate use of apportioned data is to summarize soil characteristics such as texture or OM over a region as opposed to within a single MTRS.

Table 3. 2013 Chloropicrin use by month in 3 regions; “fraction” is monthly fraction of annual total use within region.

	Siskyou		**San Joaquin Valley**		**Coast**	
Month	**Use (lbs)**	**fraction**	**Use (lbs)**	**fraction**	**Use (lbs)**	**fraction**
1	0	0.00	700	0.00	6156	0.00
2	0	0.00	36785	0.10	10044	0.00
3	6390	0.01	108211	0.28	71847	0.01
4	26023	0.05	144265	0.38	200910	0.03
5	0	0.00	10771	0.03	190111	0.03
6	0	0.00	1314	0.00	426012	0.06
7	185099	0.36	1126	0.00	555211	0.08
8	198031	0.39	302	0.00	1084033	0.16
9	86716	0.17	4131	0.01	2452710	0.37
10	5750	0.01	42015	0.11	1496688	0.23
11	0	0.00	5397	0.01	74494	0.01
12	0	0.00	28486	0.07	8514	0.00
Total	508009	---	383505	---	6576730	---

ANALYSIS

Soil temperature *"10% reduction in buffer zone distance, IF the soil temperature is measured to be 50°F or less. Record temperature measurements at the application depth or 12 inches, whichever is shallower."*

The rationale for the temperature credit is the known decrease in fumigant air-water partition coefficients and gas phase diffusion coefficients with temperature (Spurlock, 2010). Both effects should generally decrease post-application fumigant mobility and volatilization, potentially leading to reduced fumigant flux. However, degradation rates also generally decrease with temperature which may have a potentially off-setting effect. In any event, there are few, if any measured data to demonstrate the aggregate effect of low temperature on fumigant field flux.

The temperature credit would have little applicability in California under current chloropicrin application regimes. CIMIS (California Irrigation Management Information System, http://www.cimis.water.ca.gov/) data includes daily six inch deep soil temperature data for many locations. Based on those data, coastal 2011 – 2015 five year mean soil temperatures at the six inch depth are above 50°F throughout the year (Figure 1). Consequently, in this region that represents a large majority of statewide use, the temperature credit is not applicable.

In Tule Lake, Siskyou County, the 2011 – 2015 five year mean soil temperatures fall below 50°F by October 25, warming to above 50°F on March 20 (Figure 2). The corresponding dates for Merced, San Joaquin Valley, are December 10 and February 15 (Figure 2). In Siskyou County, 1.2 percent of 2013 applications occurred in the "< 50°F" window, while 3.9 percent occurred in 2014. In San Joaquin and Merced Counties, 7.5 percent of 2013 chloropicrin applications occurred during the < 50°F soil temperature time period and 1.7 percent during this same period in 2014. Thus, the temperature credit may apply for a few applications in these two regions, but based on 2013 and 2014 use data the applications represent only a small fraction of statewide use.

In addition, the percentages of applications occurring during the <50°F soil temperature time period may be somewhat overstated in the sense that cold season soil temperatures at the label-specified 12 inch depth are likely somewhat warmer than the 6 inch depth CIMIS soil temperature data used here . Deeper soil depths generally display lower annual temperature variation, and temperatures at deeper soil depths tend to the annual mean of soil temperature. This annual mean is greater than 50°F in all three of the major use regions. In summary, only a small percentage of 2013 and 2014 chloropicrin applications occurred during the <50°F time window in Siskyou County, and in the San Joaquin Valley Counties of Merced and San Joaquin.

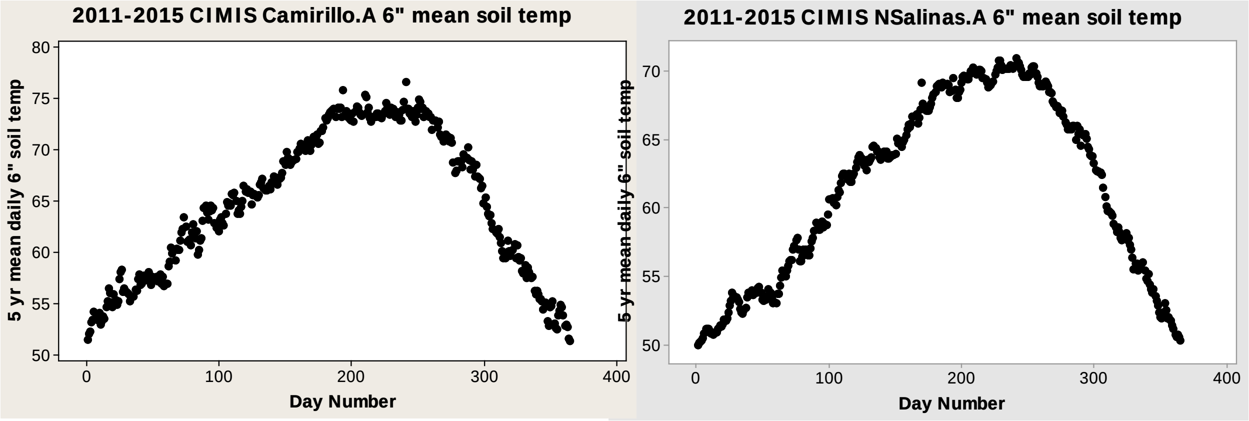

Figure 1. Mean 2011-2015 6 inch daily soil temperature (Fahrenheit) for two coastal locations. CIMIS is the California Irrigation Management Information System (http://www.cimis.water.ca.gov/).

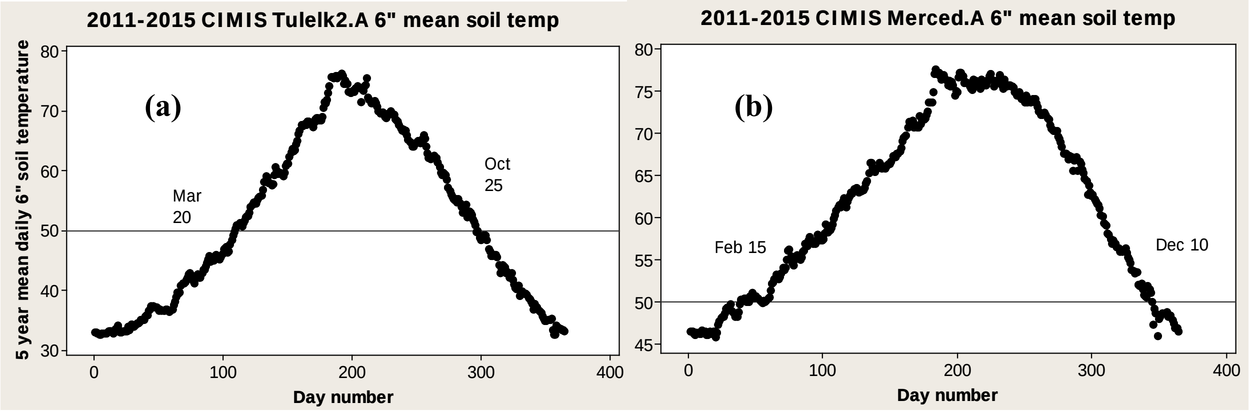

Figure 2. Mean 2011-2015 6 inch daily soil temperature (Fahrenheit) for (a) a Sisikyou County weather station and (b) a San Joaquin Valley weather station . CIMIS is the California Irrigation Management Information System (http://www.cimis.water.ca.gov/).

<u>Post-application irrigation</u> *15% reduction in buffer zone distance, IF ¼ to ½ inch of water is applied.*

The basis for this buffer zone reduction credit is the known effect of "water seals". These are post-application water applications that have been demonstrated to decrease fumigant flux in some field and laboratory studies. The supporting data for this credit was a single bedded drip study where 1/3 inch was applied over the field after application (Dawson and Smith, 2008; Dawson et al., 2011). The effect of a single small irrigation on chloropicrin flux for other application methods is uncertain (Dawson et al., 2011, p. 8). However, the USEPA buffer zone credit label language applies to *all* application methods. Here we evaluate the effect of post-application irrigations for both bare ground broadcast applications and bedded drip applications using HYDRUS 2/3D.

Bare ground broadcast application California allows untarped broadcast applications of chloropicrin, although these are uncommon. Previous studies of water seals for broadcast applications generally used multiple water applications and/or substantially more total applied water than the single "*¼ to ½ inch of water*" specified in the buffer zone reduction credit. Gao et al. (2008) applied ½ inch water immediately following fumigant application in a field study, followed by three additional applications of 0.16 inches of water at 12 h, 24 h and 48 h after application. They observed low 1,3 dichloropropene and chloropicrin fluxes relative to a non-irrigated control, but found that flux increased substantially to near control levels shortly after the last water application. Nelson et al. (2012) tested the effect of applications of ½ , 1 and 1 ½ inches of water on methyl isothiocyanate (MITC) emissions in soil columns. They found that flux reductions for the ½ inch water application were highly variable, concluding that the 1 inch applications were needed to consistently yield reduced MITC emissions.

To test the ability of a post-application water seal on bare ground broadcast chloropicrin applications as specified in the buffer zone reduction credit, I conducted simulations of shallow (12 inch) and deep (18 inch) bare ground broadcast chloropicrin applications. The vadose zone model HYDRUS 2D/3D was used to simulate maximum 6 h period mean chloropicrin flux densities (ug $m^{-2}sec^{-1}$) on a 100 lb $acre^{-1}$ (112 kg ha^{-1}) applied basis. The 6 h flux averaging periods were 00:00 – 06:00, 06:00-12:00, 12:00 – 18:00, and 18:00 – 24:00 such as would be used in a typical field monitoring study. These 6 h maximum fluxes have been historically used to determine protective buffer zones in California for different application methods. The simulation study compared the maximum 6 h fluxes from broadcast applications with post-fumigation irrigation of 3/8 inches of water to those with no irrigation.

Soil preparation prior to pre-plant soil fumigations typically entails tillage operations such as chiseling, ripping and discing, followed by irrigation to bring the soil to fumigant label-required water contents. The HYDRUS simulations here were conducted using soil water content, saturated water content and bulk density data measured in 15 California fields immediately prior to broadcast fumigation (Johnson and Tuli, 2013; Spurlock, 2015). USDA soil texture classes (e.g. sandy loam, loam, etc.) were assigned to each field based on their measured field average sand, silt and clay fractions. To accurately simulate irrigation water movement in each field, texture average soil hydraulic properties were assigned to each field using the ROSETTA pedotransfer functions (Schaap et al., 2001) as implemented in HYDRUS. Further information on the field soil properties and HYDRUS simulation details are discussed in Spurlock (2015).

The effect of the 3/8 inch post-application sprinkler irrigation was highly variable among fields, but modest in most cases (Tables 4 and 5), and particularly for the deep applications. Percent reductions in maximum 6 h flux density ranged from 4.2 percent to 28.4 percent with a mean of

11.5 percent for the shallow chloropicrin applications, while smaller reductions were found for the deep application scenario, ranging from 0.2 percent to 11.9 percent with a mean of 4.8 percent. Overall the reductions for both shallow and deep applications were much smaller than the differences between fields. For example, percent coefficients of variation for maximum 6 h flux across the 15 fields in the non-irrigated simulations were 39.2 percent and 48.9 percent for the shallow and deep applications, respectively. While the post-application irrigation reduced maximum flux in all cases, it is likely that larger water applications would provide much greater flux reductions for broadcast applications. Multiple water applications is another demonstrated method to increase water seal effectiveness for bare ground applications (Gao, 2011).

Table 4. Simulated maximum 6 h chloropicrin flux density (ug $m^{-2}sec^{-1}$, 100 lb $acre^{-1}$ applied basis) for irrigated and non-irrigated 12 inch deep applications. Difference = non-irrigated flux – irrigated flux; percent difference = (difference/non-irrigated flux)

Field	**irrigated**	**non-irrigated**	**difference**	**percent difference**
cro1	72.7	77.5	4.8	6.2%
din1	78.0	84.8	6.9	8.1%
din2	57.1	62.6	5.6	8.9%
LH1	31.2	35.6	4.4	12.4%
LH2	22.9	26.6	3.7	13.8%
LH3	22.3	24.6	2.3	9.2%
mer1	43.5	47.7	4.2	8.7%
san1	57.1	67.0	9.8	14.7%
sto1	54.7	76.4	21.7	28.4%
sto2	31.3	37.3	6.0	16.1%
vis1	45.8	47.8	2.0	4.2%
wat1	25.3	29.2	3.9	13.5%
wat2	59.3	63.2	3.9	6.2%
wat3	29.5	31.7	2.2	6.9%
wat4	47.4	55.7	8.3	14.8%
Mean	**45.2**	**51.2**	**6.0**	**11.5%**

Table 5. Simulated maximum 6 h chloropicrin flux density (ug $m^{-2}sec^{-1}$, 100 lb $acre^{-1}$ applied basis) for irrigated and non-irrigated 18 inch deep applications. Difference = non-irrigated flux – irrigated flux; percent difference = (difference/non-irrigated flux)

Field	irrigated	non-irrigated	difference	percent difference
cro1	24.2	24.4	0.2	0.9%
din1	34.2	34.2	0.1	0.2%
din2	26.1	26.9	0.8	3.1%
LH1	12.5	13.3	0.8	5.8%
LH2	7.3	8.3	1.0	11.9%
LH3	7.2	7.8	0.6	7.7%
mer1	17.9	18.4	0.6	3.1%
san1	22.9	23.8	0.9	3.8%
sto1	28.8	30.7	1.9	6.1%
sto2	11.2	12.3	1.1	9.2%
vis1	19.3	20.3	0.9	4.5%
wat1	4.6	4.9	0.3	5.4%
wat2	19.3	19.7	0.4	2.0%
wat3	9.0	9.4	0.4	4.6%
wat4	15.6	16.3	0.7	4.3%
Mean	17.33	18.04	0.7	4.8%

Bedded drip chloropicrin applications Tarped bedded drip is a common application method for chloropicrin in California strawberries. Based on discussions with applicators and researchers, a typical bed configuration for strawberries in the Salinas/Watsonville area of Monterey County is shown in Figure 3. It should be noted that other strawberry bed configurations are used in other regions of California, and also for other crops.

The configuration in Figure 3 served as the basis for the HYDRUS modeling domain used in simulations here. The drip lines were simulated as a two-dimensional line source. The TIF tarp permeability and chloropicrin soil half-life were those determined by Spurlock et al. (2013). Actual measured texture, bulk density and water content data described in the previous "*Bare ground broadcast application*" section were used to parameterize soil properties in HYDRUS. Texture class mean soil hydraulic properties were estimated for each soil using the ROSETTA module in HYDRUS. Two different drip tape flow rates were used depending on the texture class of the field being simulated. For most of the simulations a flow rate of 3 L/m h was used. For three of the finer textured soils, a lower drip tape flow rate of 1.6 L/m h was used to accommodate the lower estimated hydraulic conductivity of the soils. The drip chloropicrin application time was 4 hours (7.5 hours for the low flow simulations), followed by a 20 minute line flush to yield a total water volume applied of 13 L/m in all cases. The flow rates and application duration are comparable to those used in other studies (Qin et al., 2013; Trout et al., 2005) as well as in recently submitted registrant-sponsored bedded drip fumigation studies. For the sprinkler irrigation simulations, a sprinkler application of 0.375 inches was applied to the entire domain immediately after the drip application. The simulated sprinkler irrigation intercepted by the tarp was assumed to completely runoff to the untarped furrow, yielding net infiltration into the untarped furrow soil of approximately 1.6 inches (4 cm).

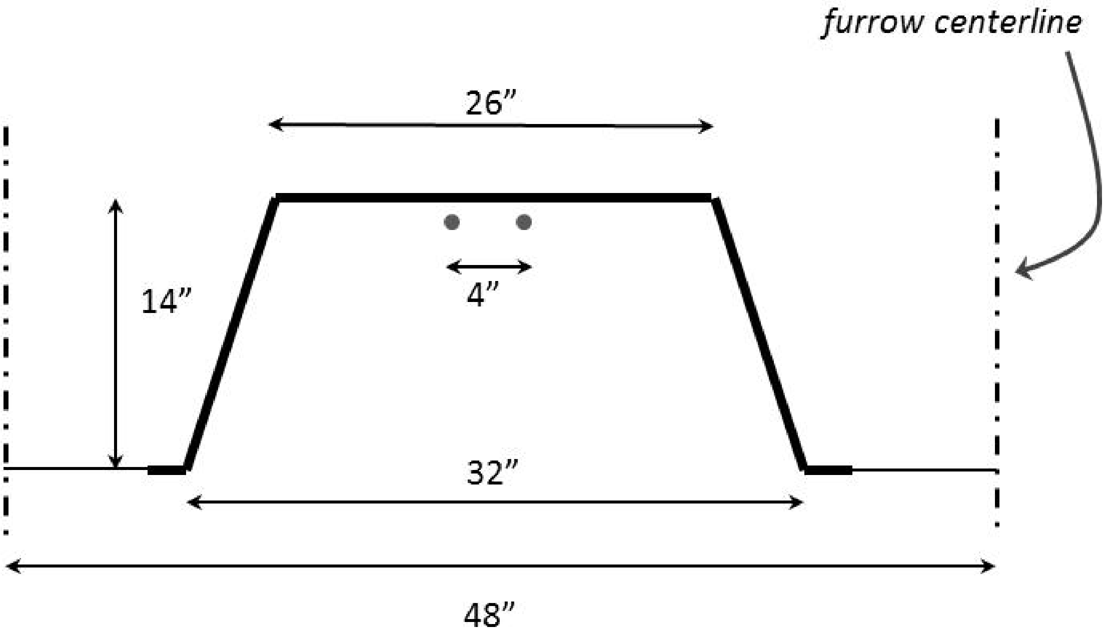

Figure 3. Bed configuration typical of strawberry production in Watsonville/Salinas area. Dimensions based on field measurements taken during an unpublished drip study. Heavy line over bed is a “totally impermeable” (TIF) tarp; untarped bare ground furrow section shown as lighter line. Tarp “tuck” at base of bed in furrow ≈ 2 inches on each side of bed. The drip lines are 1” below the bed top.

The mean cumulative volatilization in the non-sprinkler irrigated simulations of 16 % (percent of applied) compares favorably with that reported in other studies. Ajwa et al. (2009) reported cumulative chloropicrin losses from bedded drip application under TIF tarps of 23%, while Qin et al. (2013) reported cumulative chloropicrin losses of 16 % from a bedded drip application under a VIF (virtually impermeable film) tarp. DPR’s VOC emission rating for chloropicrin tarped drip applications represents the Departments estimate of expected volatilization as percent of application. That rating is 12 % (http://cdpr.ca.gov/docs/emon/vocs/vocproj/calculation_instructions.pdf, page 9). The agreement in cumulative volatilization between the non-sprinkler irrigated simulations here and other studies supports the veracity of the HYDRUS modeling procedure.

Table 6.Cumulative chloropicrin volatilization from the 15 soil profiles for nonirrigated and irrigated HYDRUS simulations of bedded drip chloropicrin applications under TIF tarp.

	Cumulative volatilization[A]	**Standard deviation (N=15)**	**Maximum[A]**	**Minimum[A]**
Nonirrigated	16.1%	5.1%	8.7%	8.6%
Irrigated	14.1%	3.5%	24.6%	20.2%

[A] percent of initial chloropicrin applied

While modest reductions were observed in cumulative volatilization due to the post-application sprinkler irrigations (Table 6), maximum 6 hr period-mean flux densities are most important. These flux densities ("flux") are the basis for estimating bystander exposures and hence, determining buffer zones. In 6 of 15 cases reductions of 20% - 30% in simulated flux were observed due to the sprinkler irrigations (Table 7). However, in 9 of 15 cases the flux reductions were on the order of 1 percent or less. The soils that yielded little or no reductions in maximum 6 hr flux were those in which the flux contribution from the untarped furrow during the maximum flux period were low. In these soils, any decrease due to irrigation had little effect on the maximum flux because the flux contribution from the furrow was already very low (e.g., Figure 4). In contrast, for those soils where the furrow makes a substantial contribution to maximum flux in the nonirrigated scenario during the maximum flux period (period 6, figure 5), irrigation can suppress the furrow contribution, thereby reducing flux. In Figure 5, irrigation causes the maximum flux period to shift to an earlier flux period (period 2). Irrigated and nonirrigated scenarios for the remaining 13 soils are provided in Appendix 2.

Several factors influence whether the furrow contributes substantially to the maximum flux period and, therefore, whether the sprinkler irrigation will decrease flux. These include (1) the initial water content of the soil, (2) the soil total porosity (i.e. saturated water content), and (3) soil hydraulic characteristics that effect both how deep water moves during the chemigation application and how fast the profile drains afterward. It is also likely that the chemigation parameters such as duration, drip line flow rate and depth of the drip line will also influence the effectiveness of the post-application irrigation on suppressing maximum flux.

Based on these simulations, the effect of a post-application 0.375" sprinkler irrigation on maximum 6 hr time-averaged flux density from bedded drip applications under TIF tarp is highly variable. While some soils showed substantial maximum flux density reductions due to sprinkler irrigation, a majority of the 15 soils showed no effect of sprinkler irrigation on maximum flux.

Table 7. Maximum 6 h period mean flux densities for non-irrigated and post-application sprinkler irrigated simulations. Fluxes (ug m^{-2} sec^{-1}) are expressed on a "whole field" basis (averaged over entire treated bed plus non-treated furrow area), and normalized to a 100 lb acre^{-1} whole field chloropicrin application basis.

		Flux density ug m^{-2} sec^{-1}		
Soil	**Drip flow rate**	**Nonirrigated**	**Irrigated**	**Percent reduction**[A]
LH1	Hi	6.0	5.9	0%
LH2	Hi	5.5	5.5	0%
LH3	Hi	5.4	5.4	0%
cro1	Hi	6.9	6.0	14%
din1	Lo	9.9	7.5	24%
din2	Hi	8.7	6.5	26%
mer1	Hi	6.4	6.4	1%
san1	Hi	7.0	6.0	14%
sto1	Hi	9.8	7.0	28%
sto2	Hi	5.9	5.9	0%
vis1	Hi	8.2	6.6	19%
wat1	Lo	4.9	4.9	0%
wat2	Hi	6.4	6.4	1%
wat3	Lo	6.1	6.1	0%
wat4	Hi	6.1	6.1	0%

[A] **percent reduction = (nonirrigated – irrigated)/nonirrigated x 100**

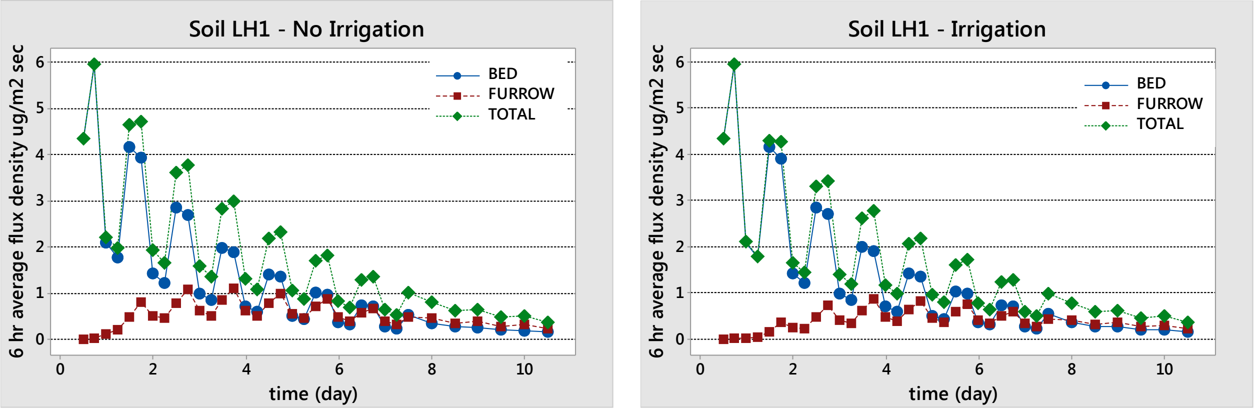

Figure 4. "No Irrigation" and "Irrigation" simulations for soil LH1. Note the minimal contribution from the furrow during the maximum flux period #2.

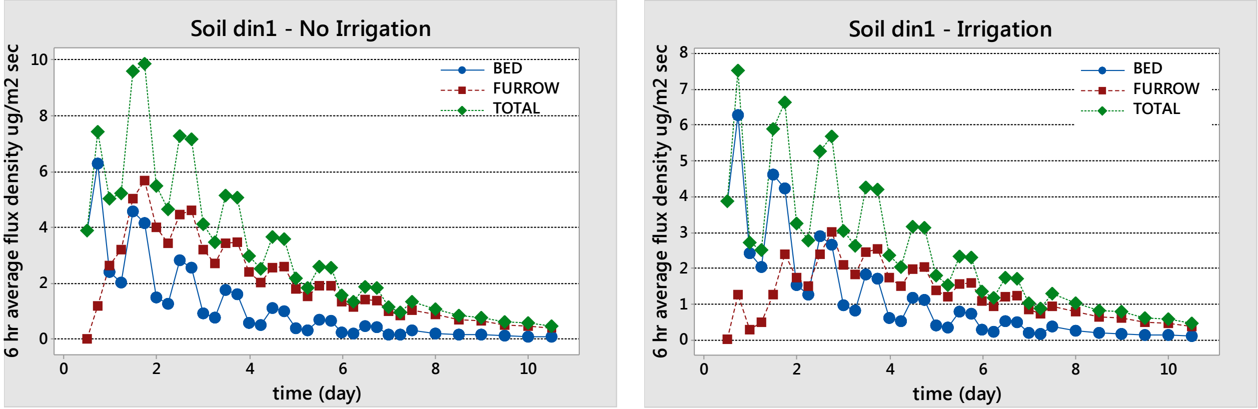

Figure 5. "No Irrigation" and "Irrigation" simulations for soil din1. Note the large contribution from the furrow during the maximum flux period #6 in the nonirrigated scenario.

<u>Soil clay content</u> *10% reduction in the buffer zone distance, IF the clay content of the soil in the application block is greater than 27%.*

The basis for this buffer zone credit is the assumption that higher clay content reflects lower soil permeability and attendant lower mobility of chloropicrin in soil. To our knowledge no field or laboratory studies have experimentally examined the effect of texture on fumigant emissions. Dawson and Smith (2008) present graphs showing modeled chloropicrin flux differences between sand, loamy sand, loam and clay loam soils, but modeling assumptions such as assumed values for soil properties for different textural classes were not provided.

The HYDRUS simulations used here to evaluate the effect of the irrigation buffer credit were conducted using DPR's measured fumigant field soil data that reflected actual field conditions as they exist after tillage and pre-irrigation immediately before fumigation (Spurlock, 2015a). We used the bare ground broadcast simulations (Spurlock, 2015a) and the TIF broadcast simulations (Spurlock, 2015b) to evaluate the clay content buffer zone credit. The soil data that were the basis for those simulations consisted of 8 fields with measured clay content < 27%, and 7 fields with measured clay content > 27%. The simulated maximum 6 hr flux density for the bare ground simulations are shown in Figure 6. There was no significant difference in maximum flux density between the "high" and "low" clay content groups (2-way analysis of variance [ANOVA], factors = clay content, depth of application; p=0.24). A similar analysis for the TIF broadcast applications (not shown) yielded *larger* fluxes from the high clay soils as compared to the low clay soils, although the difference was not significant (p=0.061).

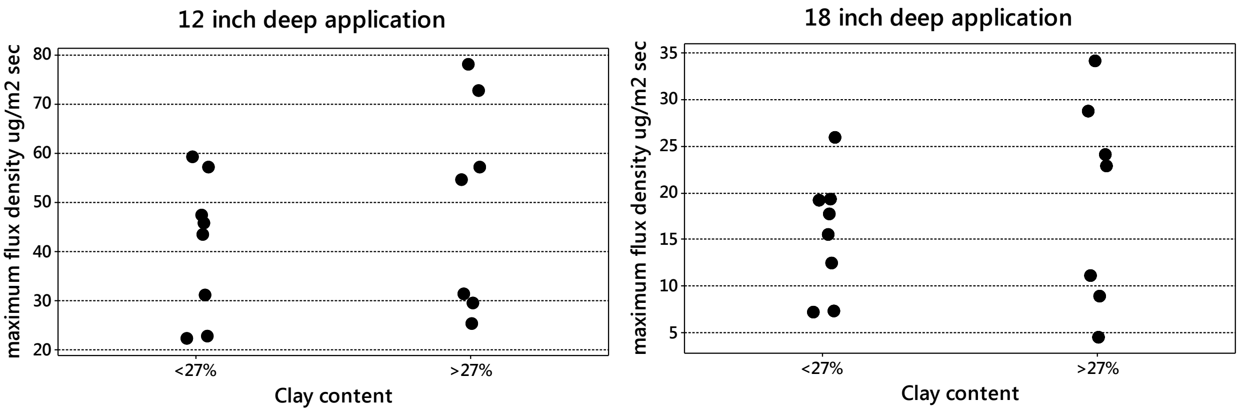

Figure 6. Individual value plots of simulated maximum 6 hr flux density (ug $m^{-2}sec^{-1}$, 100 lb $acre^{-1}$ applied basis) for bare ground broadcast simulations. Note the different Y-axis scales in the 2 plots.

The merged NRCS soil data and 2013 chloropicrin use data (e.g. Appendix 1) were used to determine the dominant soil textures in sections where chloropicrin was applied in the top 8 California counties (Table 2). Similar to the findings of Johnson and Spurlock (2009) who classified 2006 ozone season use in California's ozone nonattainment areas, soil textures in California sections where chloropicrin was applied in 2013 were dominated by coarse- and medium textured soils. Nearly ¾ of the apportioned chloropicrin use was attributable to sand, loamy sand, sandy loam and loam soils (Table 8). The "high clay" apportioned use totaled slightly less than 18 percent of total chloropicrin use in the top 8 counties, and included clay, clay loam, silty clay loam and silty clay texture classes. The category of "miscellaneous" is comprised of unclassified entries in the soil database, and includes fill land, gullied land, miscellaneous water, tidal flats, igneous rock land, bad land, terrace escarpments, beaches, pits, dumps and many others. These entries exist in the data after merging, but actual applications almost certainly don't occur in most of these.

Table 8. Apportioned 2013 chloropicrin use in the 8 high use counties by soil textural class.

Texture class	Apportioned use	Fraction of total	High clay?
sandy loam	2247943	0.30	N
loam	1733809	0.23	N
loamy sand	933411	0.12	N
misc	657922	0.09	N
sand	624418	0.08	N
clay loam	533845	0.07	Y
clay	417223	0.06	Y
silty clay loam	309072	0.04	Y
silty clay	88571	0.01	Y

Soil organic content *10% reduction in buffer zone distance, IF the organic content of the soil in the application block is > 1% - 2%; a 20% reduction in buffer zone distance, IF the organic content of the soil in the application block is > 2% - 3%; and a 30% reduction in the buffer zone distance, IF the organic content of the soil in the application block is > 3%."*

The label language for this buffer zone credit is ambiguous; soil scientists typically refer to "soil organic carbon" or "soil organic matter", but not "soil organic content". We assume here that the buffer credit language refers to soil organic matter (OM). Estimates for the OM content of different soil types are readily available from NRCS soil survey data.

We also assumed the buffer zone credit referred to native soil OM as opposed to added organic amendments; increasing the OM content of the upper 6 inches of a soil with typical bulk density of 1.5 g cm^{-3} would require incorporation of approximately 10 tons amendment $acre^{-1}$, which is impractical. In addition, the potential effect of an organic amendment would vary depending on the type of material used.

Based on the NRCS surface 0 – 10 cm soil OM data, nearly half of the apportioned chloropicrin use occurred in soils in the 2 – 3% OM range, while approximately 20% and 25% of apportioned use occurred in soils in the 0 – 1% OM and 1 - 2% OM range, respectively (Table 9). Only 5% of apportioned use was attributable to the highest buffer zone credit category of > 3% OM.

Table 9. 2013 apportioned chloropicrin use in top 8 counties by soil surface OM class.

Soil OM class	Fraction apportioned chloropicrin use
0-1%	0.21
1-2%	0.25
2-3%	0.49
>3%	0.05

To evaluate the buffer zone credit we used HYDRUS modeling. Soil organic matter content of 33 soil types where chloropicrin had been applied in the 8 high use counties (Table 2) were randomly selected. We took average soil OM estimates for the 0 - 10 cm, 10 – 30 cm and 30 - 120 cm depths for each of the 33 soils, and merged data for each soil with the bulk density, initial water content, and saturated water content data for each of the 15 fields from DPR's field variability study discussed previously (Spurlock, 2015). We also included an additional set of OM data with zero OM assumed at all depths for comparison. Thus, in total we constructed (33 +1) sets of OM data x 15 fields = 510 soil profiles for modeling.

Four application scenarios were evaluated: 12 inch deep broadcast application with bare ground, 18 inch deep broadcast application with bare ground, 12 inch deep broadcast application with totally impermeable film (TIF) tarp, and 18 inch deep broadcast application with totally impermeable film (TIF) tarp. Thus, the total number of simulations was 2040 (= 510 soil profiles x 4 application scenarios).

In all cases, increasing OM resulted in smaller simulated maximum 6 h fluxes (e.g. Figure 7). Differences in simulated maximum flux between the surface OM groups were significant for both depths of application and both TIF and bare ground surface conditions ($p < 0.01$, ANOVA not shown), (Tables 10 and 11). The differences are attributable to increased sorption of chloropicrin to soil with increasing OM, leading to decreased volatilization.

Numerous field studies were used to develop California's chloropicrin buffer zones (Barry, 2014), including many from various regions of California. Because chloropicrin use occurs in all of the different OM groupings (Table 9), it's likely that many of the studies used to develop the buffer zones also occurred in different groupings. Therefore, the current California buffer zones were likely derived using chloropicrin flux data from fields with varying OM levels. This would preclude applying a simple credit directly to current California buffer zones. USEPA addresses this issue in their field study data by using a "negative buffer zone credit" scheme to augment the buffer zones of higher OM fields (USEPA 2011, p. 6). It is not clear how USEPA implemented this procedure.

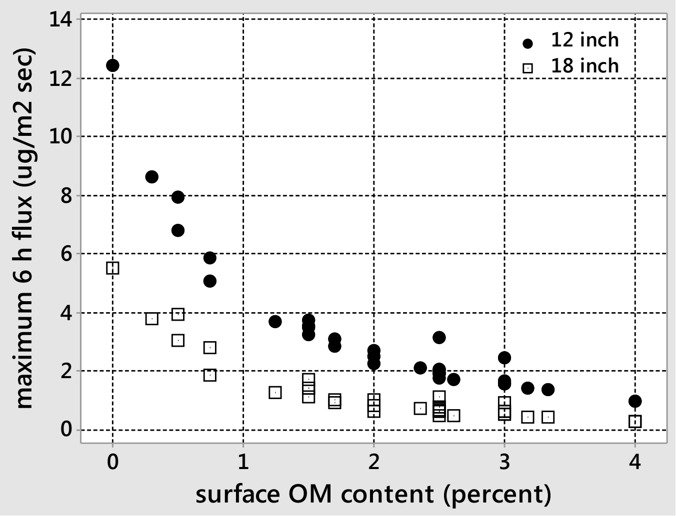

Figure 7. effect of soil OM content on maximum 6 h flux density (ug m^{-2} sec^{-1}, 100 lbs applied basis) for 12 inch and 18 inch TIF applications

Table 10. Mean and standard deviation of maximum 6 h flux density (ug m^{-2} sec^{-1}, 100 lbs applied basis) for bare ground applications.

		12 inch application depth		18 in application depth	
OM class	n	Mean of max 6 h flux	Std Dev of max 6 h flux	Mean of max 6 h flux	Std Dev of max 6 h flux
0%	1	78.6	---	27.4	---
0-1%	5	51.1	9.7	17.5	3.8
1-2%	10	24.5	3.0	9.1	2.3
2-3%	14	18.9	3.6	6.4	1.7
>3%	4	13.3	1.8	4.0	0.9

Table 11. Mean and standard deviation of maximum 6 h flux density (ug m^{-2} sec^{-1}, 100 lbs applied basis) for totally impermeable film applications.

		12 inch application depth		18 in application depth	
OM class	n	Mean of max 6 h flux	Std Dev of max 6 h flux	Mean of max 6 h flux	Std Dev of max 6 h flux
0%	1	12.4	---	5.5	---
0-1%	5	6.9	1.5	3.1	0.8
1-2%	10	3.1	0.5	1.2	0.3
2-3%	14	2.0	0.4	0.7	0.2
>3%	4	1.2	0.2	0.4	0.1

Although NRCS soil OM data are easily available, it is not clear whether the NRCS data reflect actual OM in the field. California soil surveys have been conducted over many decades, and it is unclear whether sampling was from undisturbed soils or highly cultivated fields. In addition, NRCS used several methods to estimate OM. These include both wet and dry combustion to determine organic carbon (OC), and subsequent estimation of OM using the "Van Bemmelen" factor of 1.724 g OM/g OC (USDA, 2011). In reality that factor is known to vary considerably, ranging to as high as 2.5 in some subsurface soils (USDA, 2011). In some cases mass loss on ignition has been used to estimate OM directly, especially for high OM soils (i.e., OM > 8%). Finally, OC has sometimes also been estimated from total soil carbon, and the Van Bemmelen factor then applied to estimate soil OM. Consequently the OM modeling inputs used here have considerable uncertainty. Use of actual current OC data in soils and regions where fumigations actually take place would greatly improve confidence in the modeling evaluation of this particular buffer zone credit. This could be done as a second expanded phase of the recently conducted soil variability study (Johnson and Tuli, 2013) where soil samples were collected in fields immediately prior to fumigation. In addition to analyses for water content, bulk density and texture, OC analyses would be performed. Data from such a study would also markedly improve DPR’s future fumigant modeling work generally.

CONCLUSION

The soil temperature buffer zone credit has limited applicability in California because soil temperatures generally exceed the 50°F credit cut-off in high chloropicrin use areas during most or all of the use season.

Based on HYDRUS modeling, the ¼ - ½ inch post-application irrigation buffer zone credit yields only very modest decreases in 6 hr maximum flux density for bare ground broadcast applications. Published research studies suggest use of irrigation to decrease maximum flux densities would likely require higher water applications or multiple irrigations.

The effect of the ¼ - ½ inch post-application irrigation on 6 hr maximum flux density from bedded drip applications under high barrier (TIF) tarps was highly variable across different soils. In some soils substantial reductions in flux were observed, ranging up to 28 percent. However, in more than half of the soils there was no effect of the sprinkler irrigation under the conditions simulated here. Reductions only occurred in soils where flux from the furrow made a substantial contribution during the maximum flux period. Several factors determine whether this is the case, including soil moisture content and soil hydraulic characteristics. In addition, the contribution from furrows – and hence the magnitude of any reduction due to irrigation - is likely to depend strongly on application variables, including drip line depth and total water volume applied.

The percent clay content buffer zone credit was not supported by HYDRUS simulation modeling using actual soil data collected from California fields immediately prior to fumigation. We found no significant difference in maximum 6 hr flux density for broadcast bare ground or TIF applications between soils with less than 27 percent clay and soils containing greater than 27 percent clay. In addition, the 2013 apportioned chloropicrin use data shows that less than 20 percent of soils in sections where chloropicrin is applied have clay contents greater than 27 percent.

Soil OM has an effect on flux for both bare ground and totally impermeable film broadcast applications based on the HYDRUS modeling conducted here. The 2013 apportioned chloropicrin use stratified by NRCS OM class (e.g. 0 – 1%, 1 – 2%, 2 – 3%, >3%) shows that soils from all classes exist in sections where 2013 use occurred. However, California buffer zones were likely derived using flux data collected from fields with a range of OM contents, and it would be inappropriate to apply reductions directly to buffer zones that were derived from fields with varying OM contents. Implementation of the OM buffer zone credit would require a re-analysis of the existing field studies used to support current chloropicrin buffer zones. The analysis would first determine the levels of soil OC (OM) contents in those studies, after which a a method by which credits might be applied to the "baseline" chloropicrin buffer zones would need to be developed. An additional question is whether the NRCS data accurately reflect modern soil OM contents in cultivated fields. In any event, a study to measure soil OC data from fields where fumigations take place would be very useful, both to increase confidence in model evaluations of actual potential OC (i.e. OM) effects on flux, and for future fumigant modeling efforts generally.

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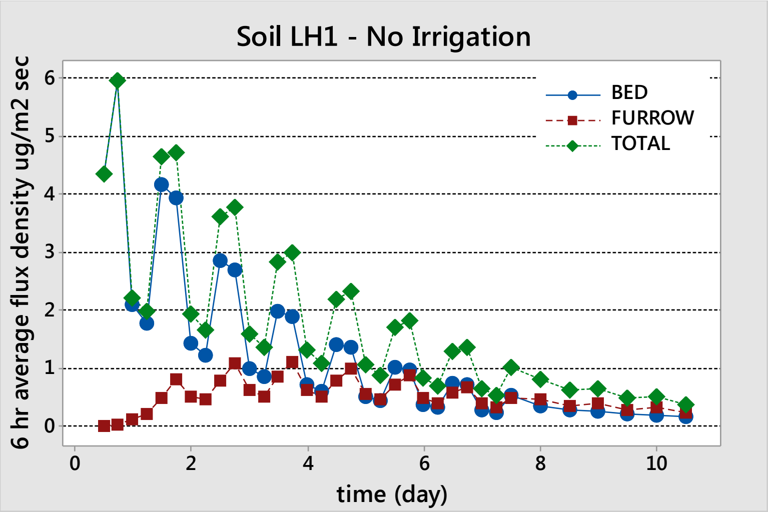
APPENDIX 1. Example record from merged soil and chloropicrin use databases.

Appendix 1. Example of merged sectional soil and use data for section S10N33W20 in Santa Barbara County. The MUID is the Map Unit Identifier (i.e. "soil type"), 2013 chloropicrin applied is in pounds, MUID area-weighted chloropicrin represents theoretical pounds for each MUID if evenly applied over entire section. Texture class was derived from MUID name, e.g. Metz loamy sand classified as "loamy sand".

MUID	Total acres in section	acres MUID in section	chloropicrin applied in section (2013)	MUID apportioned chloropicrin applied	Org. Carbon (%) 0-10cm	10-30cm	30-120cm	MUID Name	Texture
StA	638.5	60.1	44829	4222	1.74	1.74	0.82	Sorrento sandy loam, 0 to 2 percent slopes, MLRA 14	sandy loam
SuA	638.5	548.1	44829	38482	1.74	1.74	0.87	Sorrento sandy loam, sandy substratum, 0 to 2 percent slopes	sandy loam
MnA	638.5	0.2	44829	15	0.44	0.44	0.19	Metz loamy sand, 0 to 2 percent slopes	loamy sand
PsD	638.5	11.4	44829	802	0.87	0.87	0.32	Pleasanton gravelly very fine sandy loam, 9 to 15 percent slopes	sandy loam
PnA	638.5	18.6	44829	1307	0.87	0.87	0.52	Pleasanton sandy loam, 0 to 2 percent slopes	sandy loam

APPENDIX 2. Flux density time series plots for bedded drip application under totally impermeable (TIF) high barrier tarps. Simulation results shown for 15 soils, each with and without a 3/8 inch post-application sprinkler irrigation. Flux density (ug/M^2 sec) is normalized to a 100 lb/acre whole field broadcast equivalent application rate.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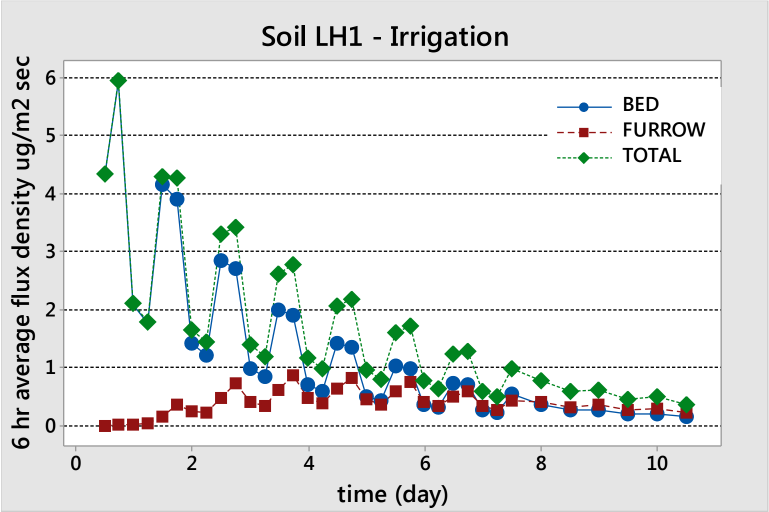
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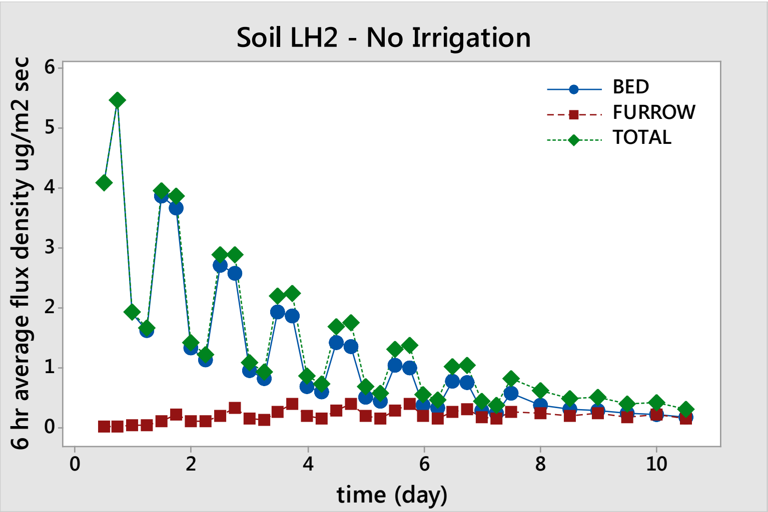
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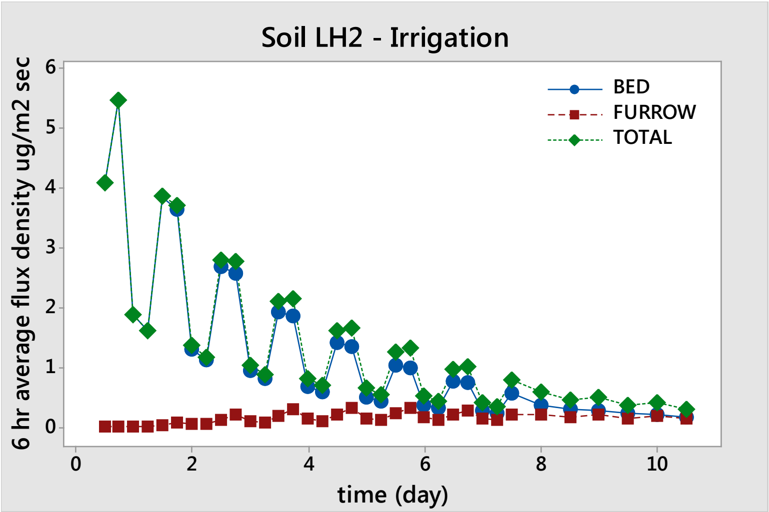
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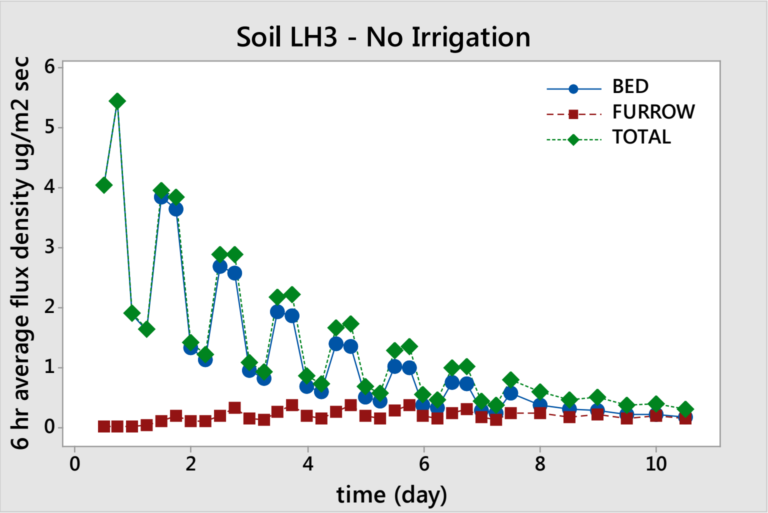
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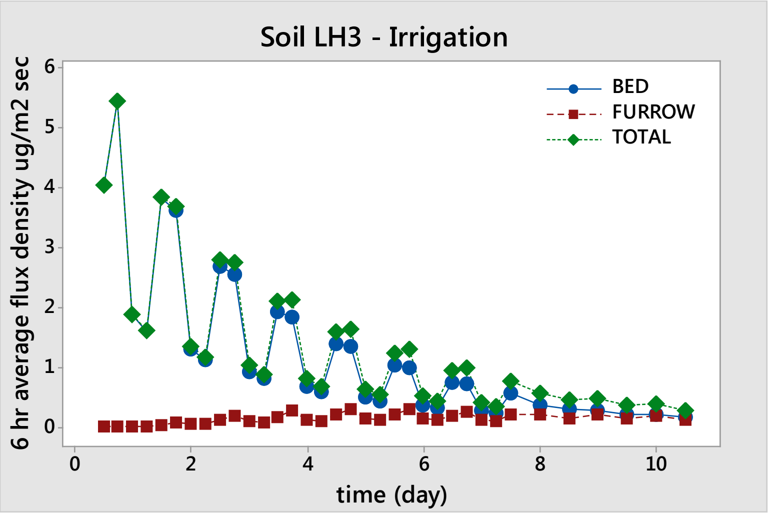
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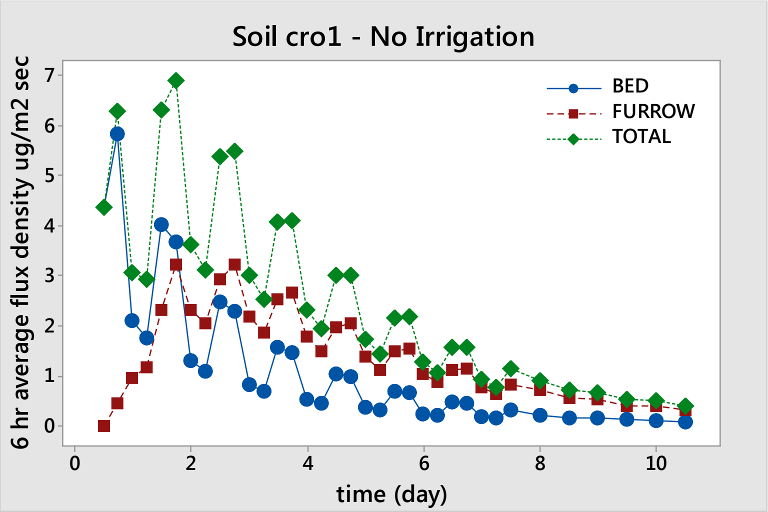
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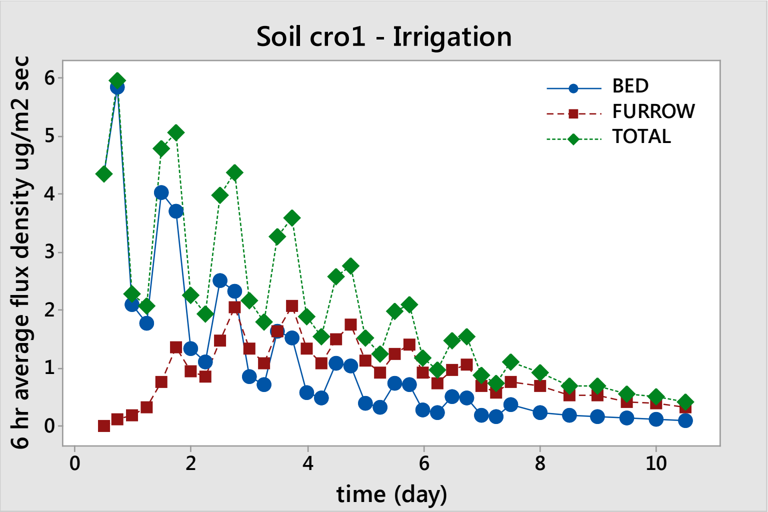
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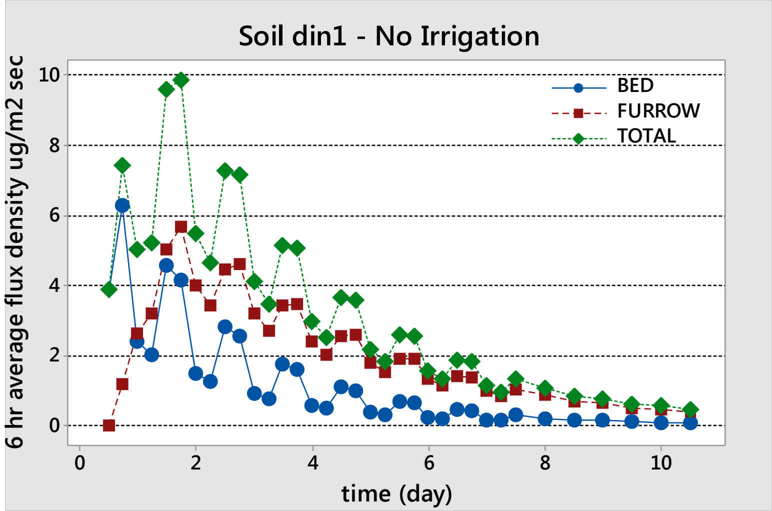
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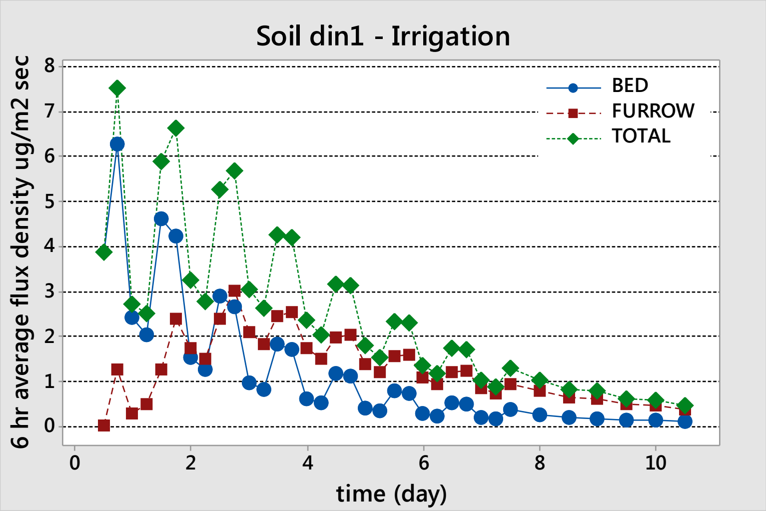
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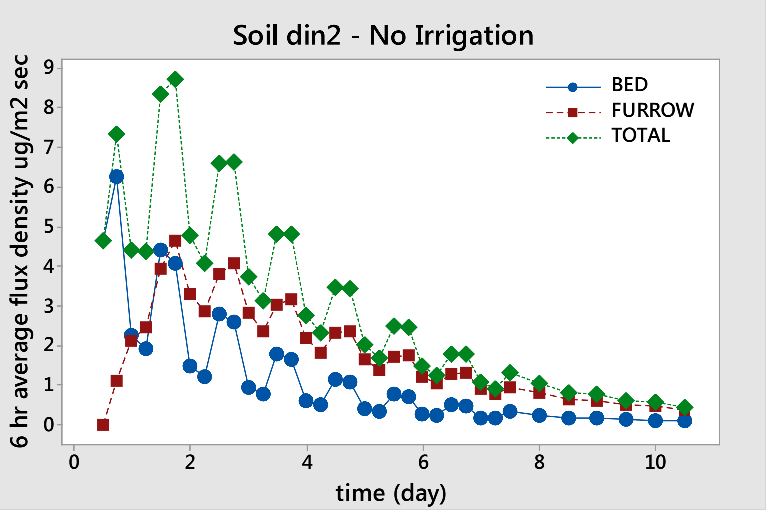
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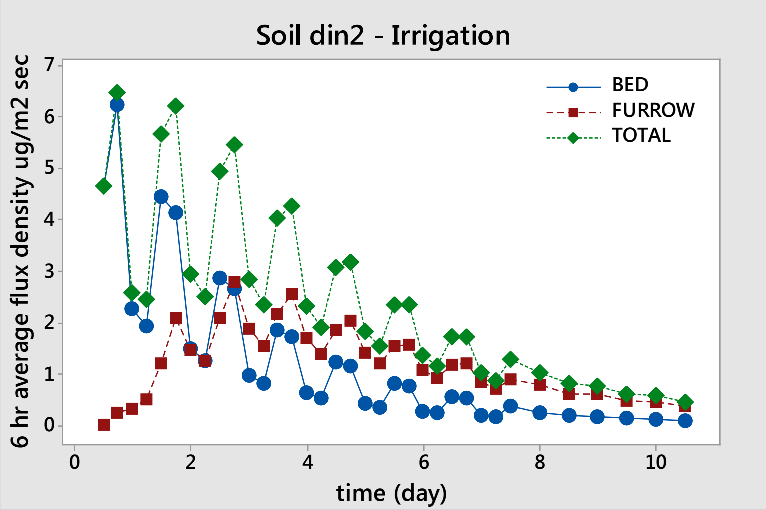
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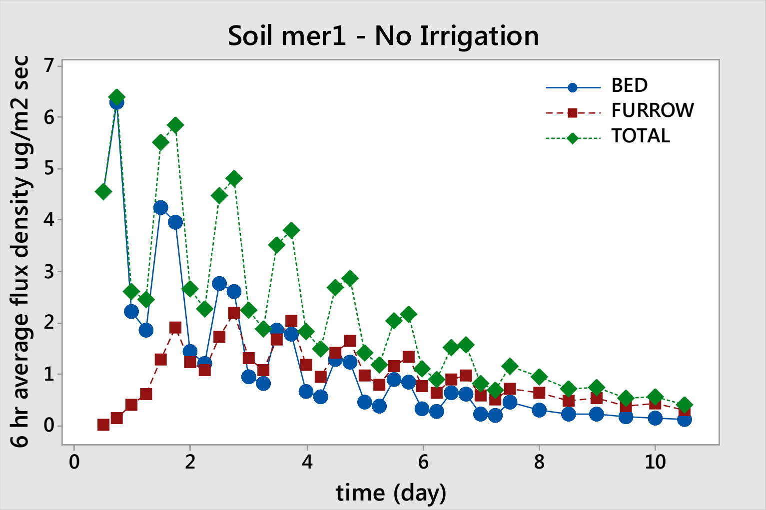

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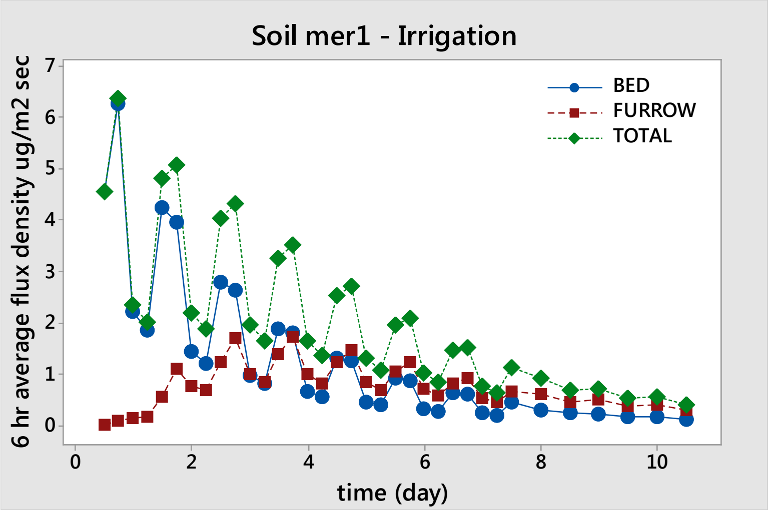

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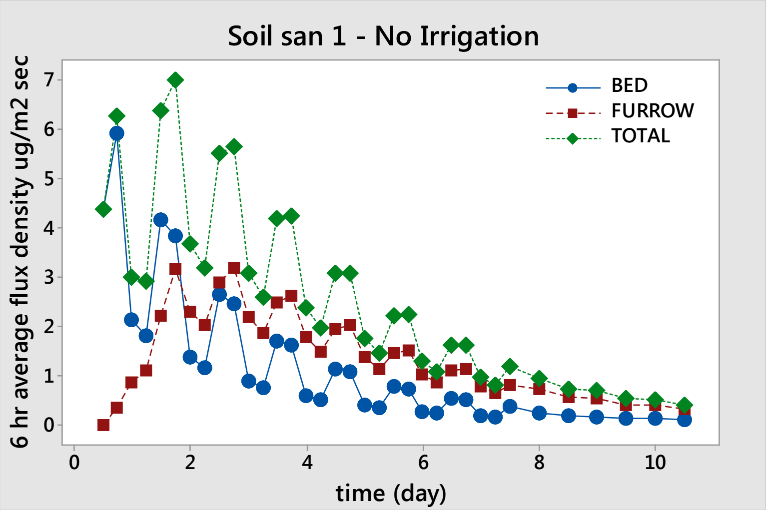

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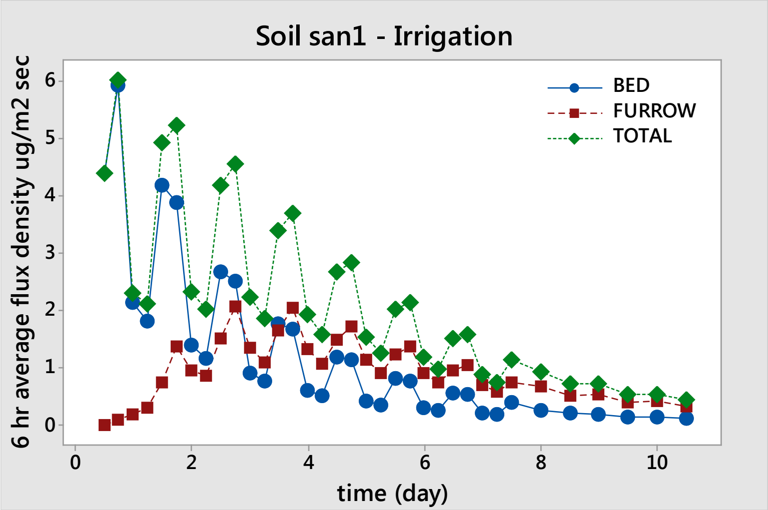

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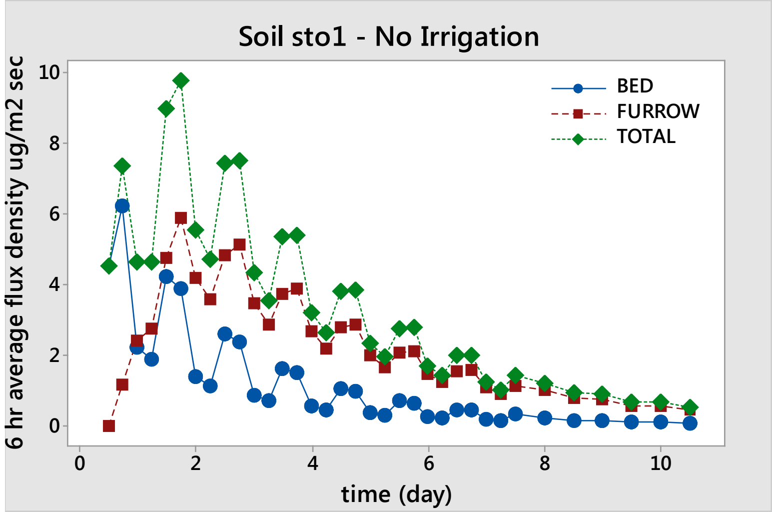
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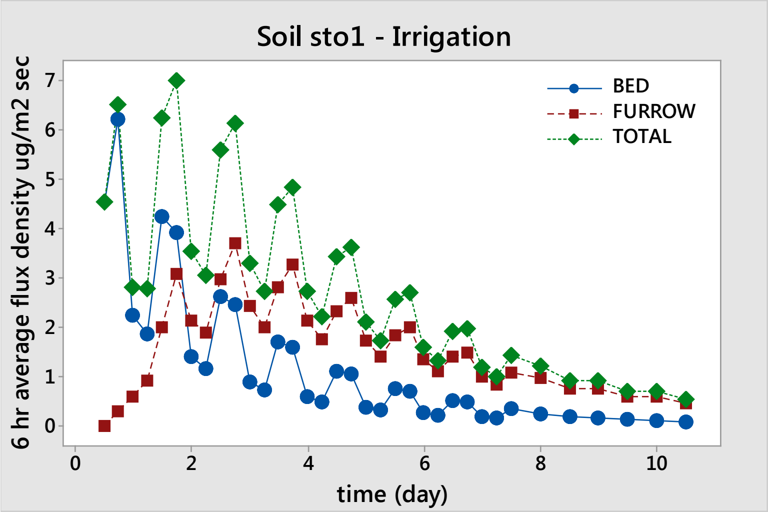
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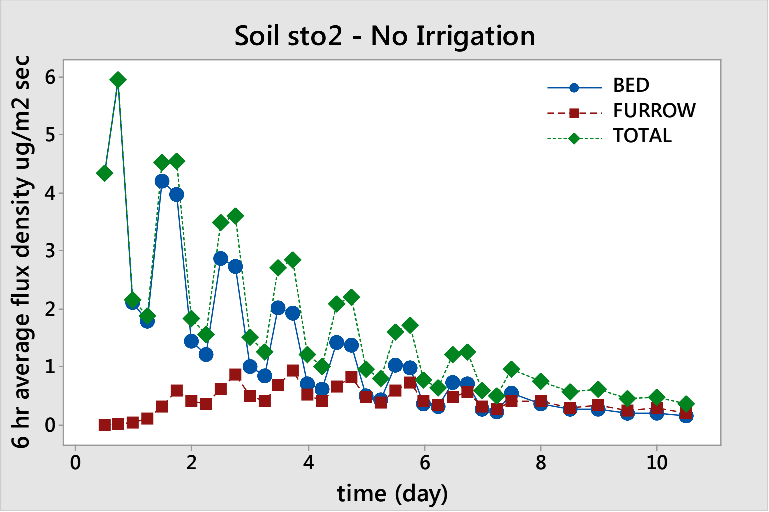
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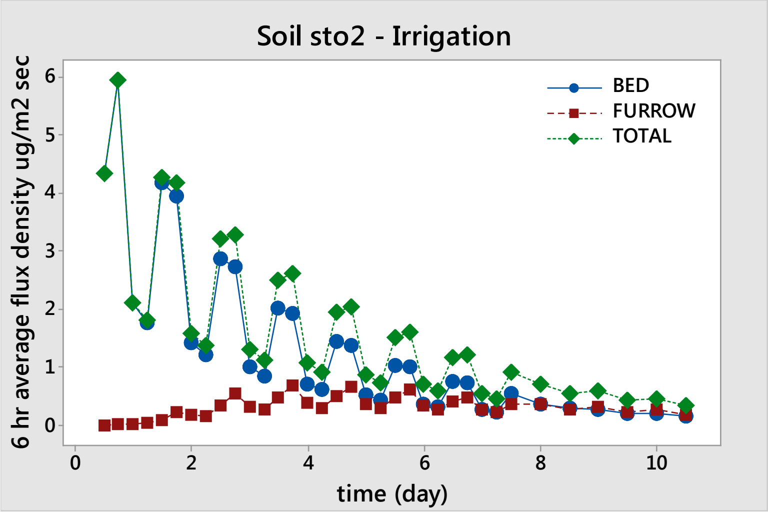
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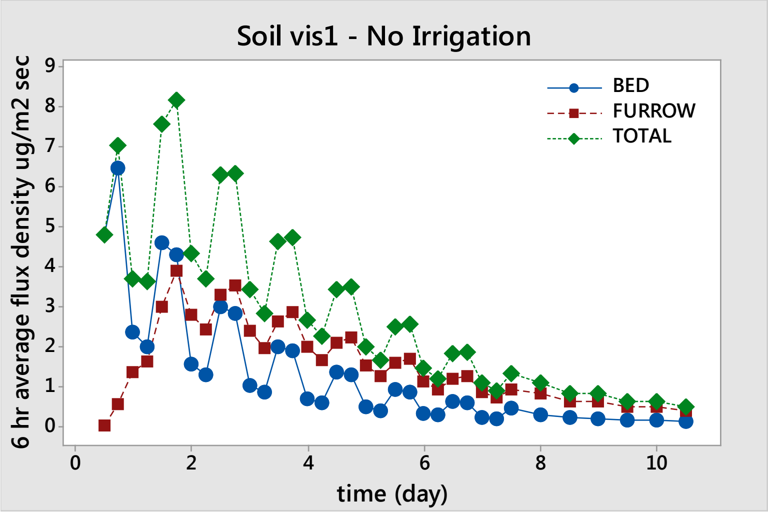
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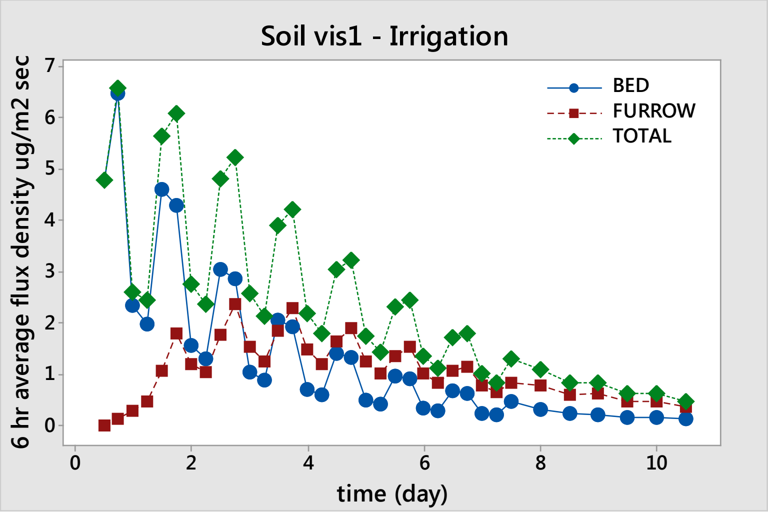
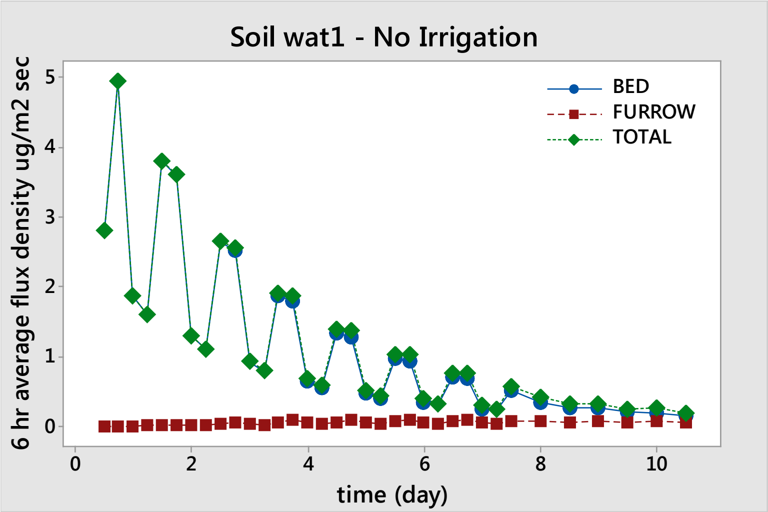
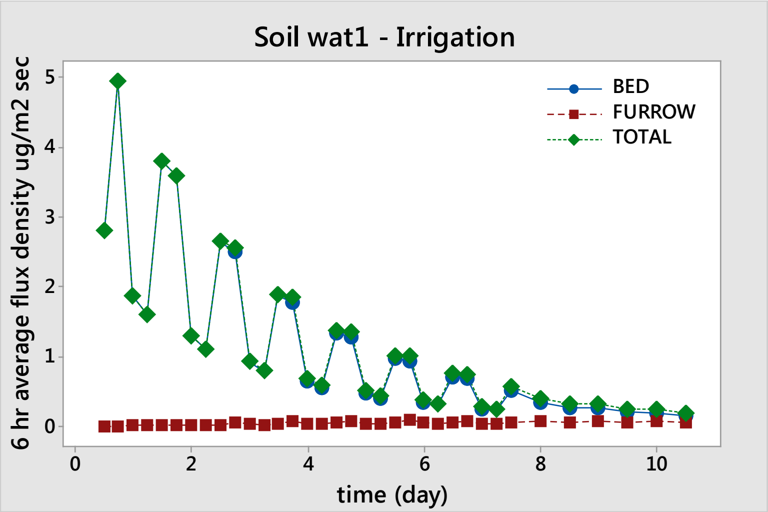
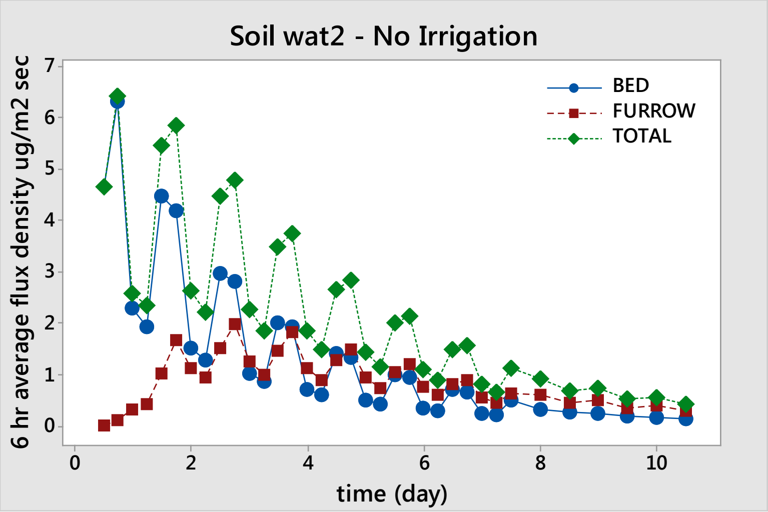
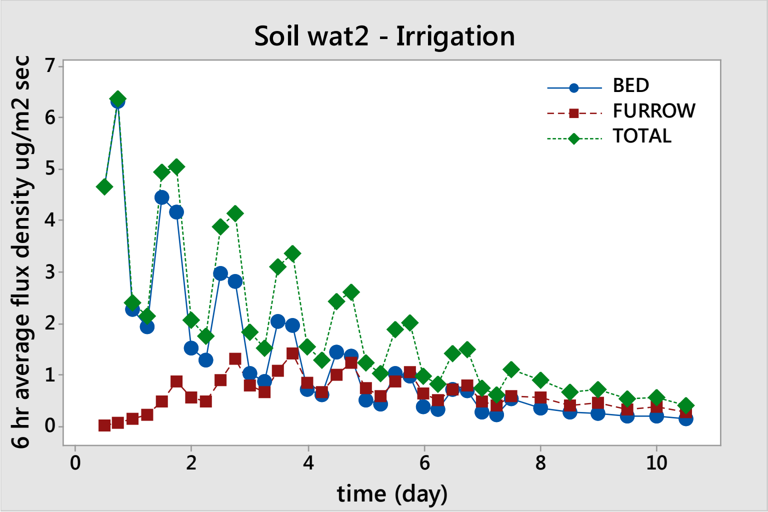
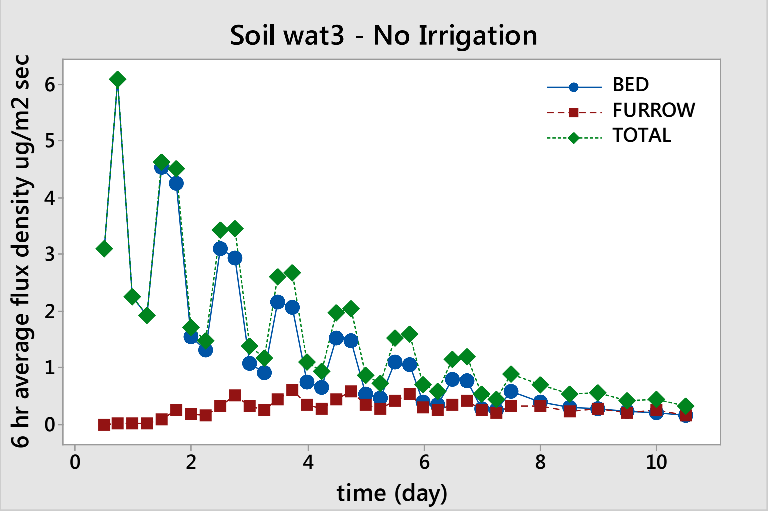

Soil vis1 - Irrigation

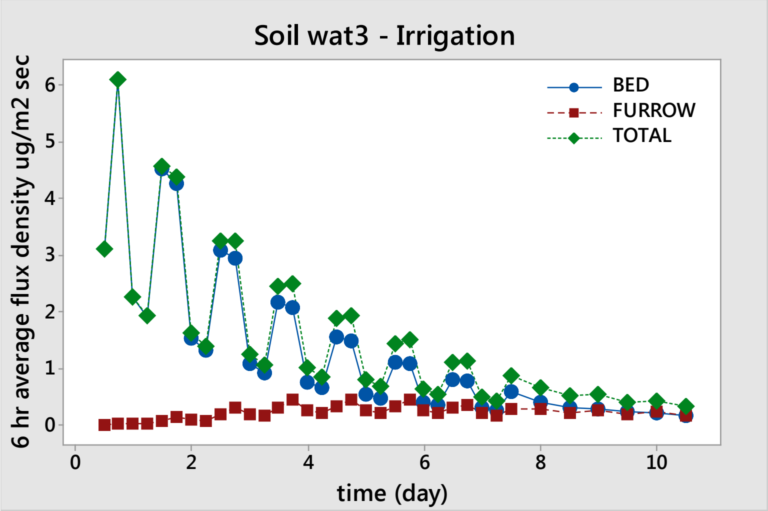

Soil wat1 - No Irrigation

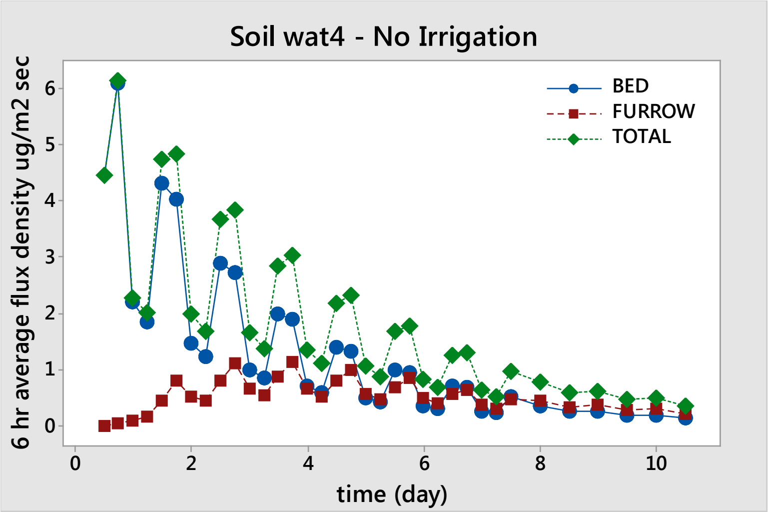

Soil wat1 - Irrigation

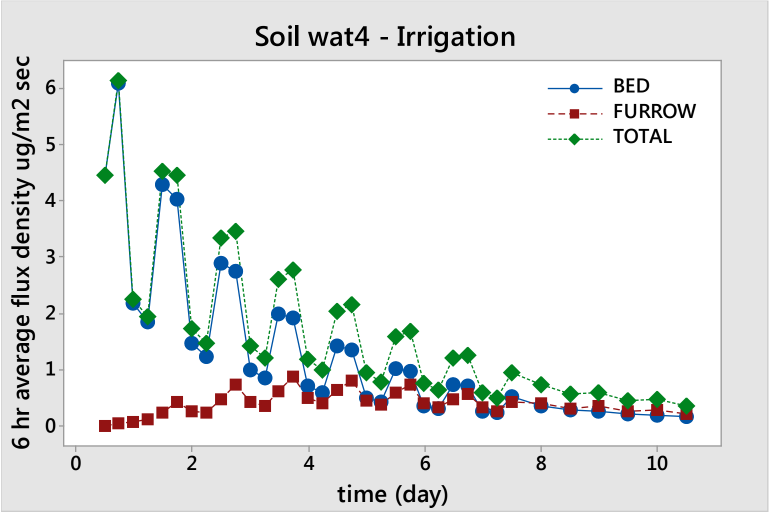

Soil wat2 - No Irrigation
6 hr average flux density ug/m2 sec
time (day)
BED
FURROW
TOTAL
0
1
2
3
4
5
6
7
0
2
4
6
8
10


Soil wat2 - Irrigation
6 hr average flux density ug/m2 sec
time (day)
BED
FURROW
TOTAL
0
1
2
3
4
5
6
7
0
2
4
6
8
10


Soil wat3 - No Irrigation
6 hr average flux density ug/m2 sec
time (day)
BED
FURROW
TOTAL
0
1
2
3
4
5
6
0
2
4
6
8
10


Soil wat3 - Irrigation
6 hr average flux density ug/m2 sec
time (day)
BED
FURROW
TOTAL
0
1
2
3
4
5
6
0
2
4
6
8
10


Soil wat4 - No Irrigation
6 hr average flux density ug/m2 sec
0
1
2
3
4
5
6
0
2
4
6
8
10
time (day)
BED
FURROW
TOTAL


Soil wat4 - Irrigation
6 hr average flux density ug/m2 sec
0
1
2
3
4
5
6
0
2
4
6
8
10
time (day)
BED
FURROW
TOTAL