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Control of off-gassing rates of methyl isothiocyanate from the application of metam-sodium by chemigation and shank injection

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Abstract

Fumigants are used to enhance the yield and quality of agricultural produce, which is critical to the maintenance of the production levels of carrots, potatoes, tomatoes, strawberries, melons, and many other crops grown in the US and throughout much of the world. With the worldwide phase-out of methyl bromide in progress, the continued availability of the remaining alternatives, such as metam-sodium, 1,3-dichloropropene, and chloropicrin, is becoming increasingly important. Metam-sodium has been used for over 40 years and is the second most widely used fumigant in the United States. Reduction in off-gassing rates of fumigants can promote health and safety benefits and an increased dose in the treatment zone, thereby increasing the potential efficacy of these products. On this basis, there is a need to evaluate off-gassing rates as a function of application and sealing methods. This paper summarizes recent research into the volatilization of the principal transformation product of metam-sodium, i.e., methyl isothiocyanate (MITC), into the atmosphere as a function of application and sealing methods. Seven field studies were conducted from 1999–2001 to evaluate the off-gassing rates of MITC from applications of metam-sodium by shank injection and chemigation using two different water sealing methods, i.e., standard water sealing and intermittent water sealing. MITC is slightly soluble in water. Irrigation of a field following an application helps to retain the compound in the soil, minimizing off-gassing while increasing the dose to the target pests. Intermittent water sealing involves applying water on an intermittent basis to minimize off-gassing rates during nighttime periods when relatively poor atmospheric dispersion conditions often occur. Research conducted by the Metam-Sodium TASK Force indicates that intermittent water sealing significantly reduces off-gassing rates both for shank injection and chemigation applications when compared with standard water sealing practices.

Keywords: Metam-sodium; MITC; Shank injection; Chemigation; Water sealing; ISCST3; Method of least squares; TOXST; Fumigants; Pesticide; Application; Agriculture; Normalized modeling; Emission fitting; Ambient monitoring

1. Introduction

The Metam-Sodium Task Force (MSTF) has conducted seven field studies over the past 3 years to evaluate off gassing of MITC from metam-sodium applications (Merricks, 2002a(2 field studies), 2001, 2002b; Sullivan et al., 2000a, b, and 2001). The more recent studies (Sullivan et al., 2001; Merricks, 2001, 2002b) included gas and liquid-phase methyl isothiocyanate (MITC) analysis within the soil in the treatment zone, in addition to monitoring MITC in the ambient air surrounding the field. Studies conducted in 2001 also included a biological component to assess the effectiveness of alternate application and sealing methods on the control of nematodes. Four of these field studies

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Abbreviations: MSTF—metam-sodium task force; MITC—methyl isothiocyanate; VIF—virtually impermeable film

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(Merricks, 2001, 2002a, b) meet the requirements of Good Laboratory Practice (GLP) standards as defined by the Code of Federal Regulations promulgated by the US Environmental Protection Agency (Federal Register, 1988, 40 CFR 160). The remaining research constituted pilot trials aimed at guiding further research. The measured concentrations, when interpreted using dispersion modeling normalized to $1\,\mu g\,m^{-2}\,s^{-1}$, can provide an estimate of off-gassing rates of MITC as a function of time following an application and as a function of application method. These data then can be used to help identify methods to reduce off-gassing rates, as well as to support quantitative exposure and risk assessment via atmospheric dispersion modeling.

2. Baseline field studies

The conversion of metam-sodium to MITC, the subsequent fate of MITC within the soil (gas and water phase), and the release of MITC to the atmosphere are dependent on many variables, including soil type, soil pH, soil moisture, soil temperature, atmospheric wind speed, and the complex interactions at the soil–atmospheric interface on a diurnal basis (Van den Berg et al., 1999; Van den Berg, 1992, 1993; Woodrow et al., 2001). Based on research conducted to date, the greatest potential for off-gassing (field loss through volatilization) can be expected during the following conditions: a sandy relatively dry soil and meteorological conditions that are conducive to rapid drying of the soil surface and increased vapor pressures for MITC, e.g. moderate to high wind speeds and hot air temperatures at the surface (Van den Berg, 1992).

The conditions, as described above, were associated with most of the days for these field studies (Merricks, 2001, 2002a, b; Sullivan et al., 2000b, 2001). On this basis, it would be expected that computed off-gassing rates from these studies represent high-end off-gassing rates. Emission rates developed for these studies can be used to conservatively represent heavier soils and cooler conditions until the scope of available research includes broader coverage of soil types and soil temperature conditions.

Two field studies were conducted in June 1999 to establish baselines concentrations using traditional metam-sodium application and water sealing methods (Merricks, 2002a). These studies involved applications in Kern County, CA for shank injection and chemigation applications at the maximum allowable label rate of 75 gallons per treated acre. The fields, 80-acres in size, were applied with metam-sodium on a commercial scale for carrots.

For the shank injection application, two shank injection rigs applied metam-sodium simultaneously over an approximately 6-h period. Three injectors per bed were set at 6, 10, and 16 in below the surface of pre-formed beds, with a horizontal spacing of 13.3 in. The pre-formed beds occupied approximately 50 percent of the total acreage. Standard water sealing methods were used, i.e., $\frac{1}{4}$ in of water per hour over a 2-h period, starting shortly (<1 h) following the passage of the injectors.

The chemigation application was sequenced over 4 days, applying 20 acres per day, consistent with common practice. Approximately 1.5 acre-inches of water were applied for each set over the 6-h application periods. Standard water sealing methods were used, i.e., $\frac{1}{4}$ in of water per hour over a 2-h period, starting immediately at the completion of application.

Table 1
Soil characteristics

Soil characteristic	Chemigation site	Shank injection site[a]
% Sand	75	77
% Silt	16	17
% Clay	9	6
USDA, classification	Sandy loam	Sandy loam
Bulk density	1.32	1.37
Particle density	2.42	2.60
Porosity	45.3	47.3
% Soil moisture at $\frac{1}{3}$ Bar[b]	10.1	9.5

[a] These values are averaged from two soil surveys conducted at the site.

[b] Soil samples collected on 6/1/99 prior to both applications.

The soil characteristics for both studies are summarized in Table 1. Sky conditions were clear throughout both field studies, with hot daytime temperatures (maximum afternoon temperatures ranging from 86.5–105.7°F) and moderate afternoon wind speeds (e.g., range was $0.5–3.9\,m\,s^{-1}$, average $2.3\,m\,s^{-1}$). The nighttime periods were associated with light wind speeds (e.g., range was $0.0–1.6\,m\,s^{-1}$; average $0.5\,m\,s^{-1}$) and the atmosphere were classified as atmospherically stable (based on Pasquill/Gifford stability classifications; Gifford, 1976) throughout the nighttime periods of the 4-day studies.

3. MITC sampling and analytical methods

Figs. 1 and 2 show the air quality monitoring networks and meteorological weather stations established in the vicinity of both of the applied fields. Air quality samples for MITC were collected on activated charcoal tubes (400 mg front sections/200 mg back sections) at a flow rate of $1\,l\,min^{-1}$. Calibration of the flow rate was confirmed during each sample change-out using rotameters. Samples were collected on a 4-h basis

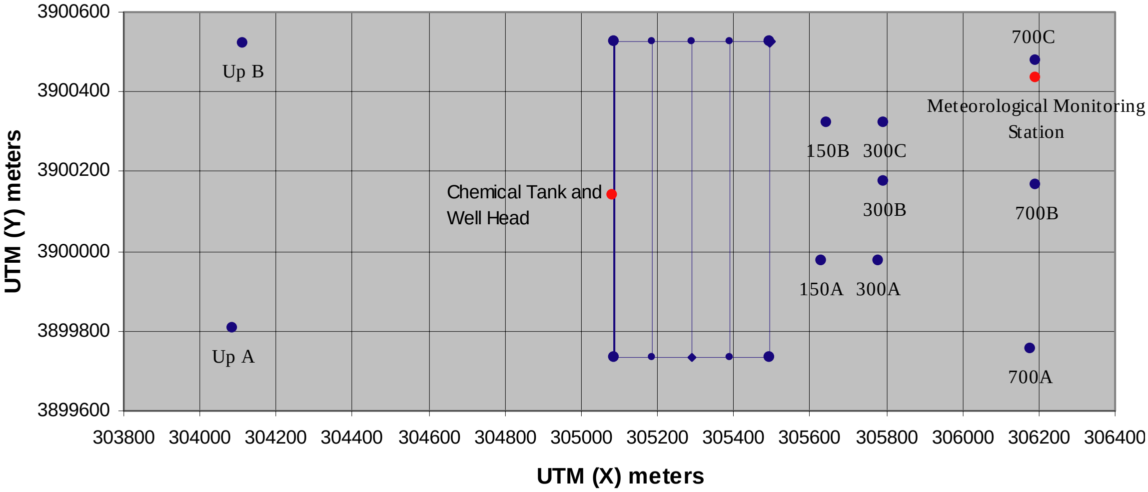

Fig. 1. Kern 1999 (Merricks, 1999) chemigation site and surrounding receptors. Blue dots represent the locations of the monitoring stations at 150, 300, 700, and 1000 m from the edge of the field.

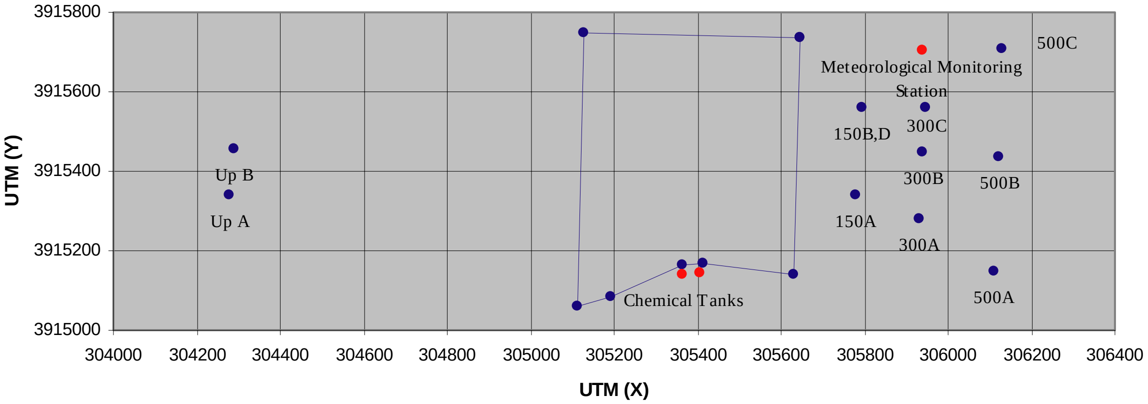

Fig. 2. Kern 1999 (Merricks, 1999) shank injection site and surrounding receptors. Blue dots represent the locations of the monitoring stations at 150, 300, 500, and 800 m from the edge of the field.

during the 4-day period post application (i.e. 24, 4-h periods for each study).

MITC air sampling charcoal tubes were stored on ice immediately after removal from the field, transferred to storage on dry ice at the completion of each collection period, and then shipped to the analytical laboratory under dry ice for analysis at the conclusion of each field study. Samples were then stored in the laboratory at a temperature of -20 ± 5°C prior to analysis.

Contents of the charcoal tubes were transferred to glass vials (combined front and back sections per method validation; Merricks, 2002a), mixed with an ethyl acetate solution containing 20 percent carbon disulfide (CS_2), and stored overnight at ambient temperature. An aliquot of the extract was transferred to a vial and analyzed by gas chromatography using a Shimadzu NPD GC detector with a methyl 50 percent phenyl silicone column.

4. Meteorological data collection methods

Onsite meteorological data were collected, consistent with the requirements of GLP, including the wind speed and wind direction data at 2 and 10 m levels, vertical wind speed at 10 m, ambient temperature at 2 and 10 m, and relative humidity at 2 m. Meteorological data were stored on a minute-by-minute basis to support subsequent interpretation, and averaged on an hourly basis as direct input to the dispersion modeling analyses that were used to estimate emission rates. In order to compute a valid mean hourly wind direction (θ), the following equation was used to account for wind direction discontinuities due to the circular function of the wind direction (1–360°; US EPA, 2002):

$$\theta \equiv 1/N \sum_{1}^{N} D_i, \tag{1}$$

$$\begin{aligned}
&D_i = \theta_i \quad \text{for } I = 1,\\
&D_i = D_{i-1} + \delta_i + 360 \quad \text{for } \delta_i < -180 \text{ and } I > 1,\\
&D_i = D_{i-1} + \delta_i \quad \text{for } |\delta_i| < 180 \text{ and } I > 1,\\
&D_i = D_{i-1} + \delta_i - 360 \quad \text{for } \delta_i > 180 \text{ and } I > 1,\\
&D_i \text{ is undefined for } \delta_i = 180 \text{ and } I > 1,\\
&\delta_i = \theta_i - D_{i-1} \quad \text{for } I > 1,
\end{aligned}$$

where, θ_i is the azimuth angle of the wind vane for the ith sample.

5. Air dispersion modeling methods

The US Environmental Protection Agency's (US EPA) dispersion model, the Industrial Source Complex model short-term mode (ISCST3; US EPA, 1995, 1999), was used to compute normalized model concentrations at the location of each monitoring site and for each specific sampling period. The monitoring sites and the corners of the respective fields were determined by a global positioning system (GPS) and input to the model applications. The rural regulatory mode of ISCST3 was selected for the modeling runs. Area sources were used to represent the off-gassing fields with sizes based on the GPS data. The normalized model estimates were computed using emission rates normalized to $1\,\mu\text{g}\,\text{m}^{-2}\,\text{s}^{-1}$ for the complete application area,[1] and matched to the meteorological conditions collected onsite during each of the 4-h air quality sampling periods (based on methodology developed in Johnson et al., 1999).

6. Statistical analytical methods

For normalized data, the best-fit estimate for determining the slope of a line between two variables is to use the method of least squares. This procedure fits the line with a zero intercept, which provides more parsimonious estimates of emission distributions and promotes more effective use of the typically small sample sizes available to estimate emission rates for each period. The zero intercept assumption is consistent with generally observed background concentrations for MITC, which are generally $\leqslant 1$ ppb ($3\,\mu\text{g}\,\text{m}^{-3}$; Krieger and Dinoff, 1999; Lompoc Interagency Work group, 1999), i.e. negligible relative to measured concentrations observed near the applied fields shortly following application, i.e. approximately 100 times or more smaller than peak measured concentrations and close to zero. Considering that a near-zero intercept is expected, limiting the fitted parameter to only the slope is consistent with the relatively small sample sizes (8–15 sampling sites).

The observed (measured) concentrations were placed on the "y" axis and modeled concentrations on the "x" axis. The general method of least squares is as follows:

$$\text{Slope} = \sum (x_i y_i) / \sum (x_i^2),$$

where x_i is the normalized modeled concentrations ($\mu\text{g}\,\text{m}^{-3}$) for the 4-h averaging period being fit and y_i the measured concentrations ($\mu\text{g}\,\text{m}^{-3}$) matched to monitoring sites for the 4-h averaging period being fit.

Estimated emission rates for each sampling period were computed as follows:

$$\text{Emission rate } (\mu\text{g}\,\text{m}^{-2}\,\text{s}^{-1}) = (1.0\,\mu\text{g}\,\text{m}^{-2}\,\text{s}^{-1}) \times (\text{slope}).$$

The following specific fitting procedure is based on the adaptation of the above method of least-squares. The residuals of the method of least-squares emission fits, based on the natural log transformation of the measured and modeled data, were reviewed. The results showed that the residuals generally met the normality test based on the Shapiro–Wilk and Kolmogorov–Smirnoff tests and were reasonably consistent with the assumption of homogeneity of the variance.

In applying the natural log transformation, a constant factor of 0.75 was applied to the measured and modeled concentrations prior to transformation to minimize artifacts near zero (Berthouex and Brown, 1994). In addition, measured and modeled concentrations that were $<0.1\,\mu\text{g}\,\text{m}^{-3}$ were set to $0.1\,\mu\text{g}\,\text{m}^{-3}$ to promote consistency with the minimum measured concentration of $0.1\,\mu\text{g}\,\text{m}^{-3}$, i.e., one-half of the detection limit.

The method of least-squares computed slope in natural log space was then multiplied by the modeled results for each receptor for the 4-h averaging period under review. The residuals of the modeled concentrations and measured concentrations for each receptor in

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[1] The shank injection application was completed for the full application area during the first 6 h of the study. The chemigation study, on the other hand, was a sequential application with the size of the applied field increasing during each of the 4 days of the study (20 acres per day applications; Merricks, 2002a). The first six periods of the chemigation study (i.e. the first 24-h after the start of the application), therefore, provides the most direct basis to directly estimate emission rates based on only one off-gassing 20-acre field. For each subsequent day, as the applied area increased, the emission rate was calculated based on the newly applied area plus the area already applied as a conservative default. Future studies were based on single application sets.

natural log space were then squared. Finally, the experimental error variance, variance of the slope, and standard error of the estimate were calculated by the following formulae which were used to calculate the best estimate for the emission rate in normal space (Berthouex, 1994):

Measured value in natural log space ($y_{\ln i}$) = ln ($y_i + 0.75$),

Normalized modeled value in natural log space ($x_{\ln i}$) = ln ($x_i + 0.75$),

Slope in natural log space ($S_{\ln}$) = $\sum (x_{\ln i} \times y_{\ln i})/\sum (x_{\ln i})^2$,

Best estimate of the modeled value in natural log space ($x_{\ln j}$) = $S_{\ln} \times x_{\ln i}$,

Experimental error variance (E_{v}) = $\sum (x_{\ln j} - y_{\ln i})^2/(N-1)$,

Variance of the slope (V) = $E_{\mathrm{v}}/(x^2_{\ln i})$,

Standard error of the estimate computed in natural log scale ($\mathrm{SE_b}$) = $V^{0.5}$,

Best estimate (median) emission rate in original units = EXP($S_{\ln} + 0.5\ \mathrm{SE}_{\mathrm{b}}^2$), where, x_i is the normalized modeled values, y_i the measured values and N the number of sample pairs.

Tables 2 and 3 present a summary of estimates of emission rates for all periods associated with the baseline studies (standard water sealing methods; Merricks, 2002a). The emissions assessment results are presented using the natural log-normalized method of least squares or default methods as described below. Review of the data from the available studies revealed that datasets with standard errors of the estimate >1.5 were not well represented using the natural log-transformed method of least squares. Default methods, therefore, were used as shown in Table 4. The majority of the emission rates were estimated by the natural log-normalized method of least squares based on natural log-normalized measured and modeled data.

Table 4 explains the basis to select between the weighted linear interpolation and the measured/modeled default methods. The default method identified in Tables 2 and 3 as the weighted linear interpolation method was used based on the nearest non-defaulted periods for periods where the number of valid pairs were less than three, where a valid pair is defined as both modeled and measured concentrations $>0.1\,\mu\mathrm{g\,m^{-3}}$. Because 4-h averaging is used in this method, the potential for mismatches on a diurnal basis were minimized when using this default method.

For the measured/modeled default method, the mean of all measured concentrations divided by the mean of all modeled concentrations in the receptor network (with values $<0.1\,\mu\mathrm{g\,m^{-3}}$ set to $0.1\,\mu\mathrm{g\,m^{-3}}$) was used as a default to estimate the median emission rate.

Table 2
Kern 1999 Chemigation standard seal study (Merricks, 2002a)[a]

Period	Standard error	Valid pairs	Emissions calculation method used	Final emission rate
7:30–11:30	0.52	⩾3	Log-normalized	177.65
11:30–15:30	**3.11**	1	Interpolation	151.44
15:30–19:30	**4.19**	1	Interpolation	125.23
19:30–23:30	0.69	⩾3	Log-normalized	99.02
23:30–3:30	0.63	⩾3	Log-normalized	60.10
3:30–7:30	**3.15**	⩾3	Measured/modeled	387.09
7:30–11:30	0.41	⩾3	Log-normalized	17.66
11:30–15:30	**2.03**	1	Interpolation	24.71
15:30–19:30	**1.78**	1	Interpolation	31.75
19:30–23:30	0.93	⩾3	Log-normalized	38.80
23:30–3:30	0.61	⩾3	Log-normalized	36.10
3:30–7:30	0.30	⩾3	Log-normalized	5.64
7:30–11:30	**2.98**	⩾3	Measured/modeled	85.08
11:30–15:30	**2.12**	1	Interpolation	63.38
15:30–19:30	0.43	2	Interpolation	41.68
19:30–23:30	0.60	⩾3	Log-normalized	19.99
23:30–3:30	0.18	⩾3	Log-normalized	7.41
3:30–7:30	0.18	⩾3	Log-normalized	8.42
7:30–11:30	0.48	⩾3	Log-normalized	52.95
11:30–15:30	1.41	1	Interpolation	39.65
15:30–19:30	1.25	1	Interpolation	26.35
19:30–23:30	0.16	⩾3	Log-normalized	13.04
23:30–3:30	0.07	⩾3	Log-normalized	7.91
3:30–7:30	0.41	⩾3	Log-normalized	14.76

[a] Times are in Pacific Daylight Savings Time.

Table 3
Kern 1999 shank injection standard seal study (Merricks, 2002a)[a]

Period	Standard error	Valid pairs	Emissions calculation method used	Final emission rate
6:30–10:30	0.39	$\geqslant 3$	Log-normalized	21.55
10:30–14:30	1.49	$\geqslant 3$	Log-normalized	74.22
14:30–18:30	0.88	$\geqslant 3$	Log-normalized	36.07
18:30–22:30	1.45	$\geqslant 3$	Log-normalized	83.42
22:30–2:30	0.92	$\geqslant 3$	Log-normalized	24.46
2:30–6:30	**1.67**	2	Interpolation	22.56
6:30–10:30	1.22	0	Interpolation	20.66
10:30–14:30	0.45	$\geqslant 3$	Log-normalized	18.76
14:30–18:30	0.53	$\geqslant 3$	Log-normalized	11.23
18:30–22:30	0.71	$\geqslant 3$	Log-normalized	56.86
22:30–2:30	**2.73**	$\geqslant 3$	Measured/modeled	299.06
2:30–6:30	**3.68**	1	Interpolation	151.53
6:30–10:30	0.65	$\geqslant 3$	Log-normalized	4.00
10:30–14:30	0.22	$\geqslant 3$	Log-normalized	4.63
14:30–18:30	0.13	$\geqslant 3$	Log-normalized	3.23
18:30–22:30	0.22	$\geqslant 3$	Log-normalized	10.02
22:30–2:30	1.11	$\geqslant 3$	Log-normalized	23.42
2:30–6:30	**5.14**	1	Interpolation	14.34
6:30–10:30	0.94	$\geqslant 3$	Log-normalized	5.27
10:30–14:30	0.37	2	Interpolation	4.05
14:30–18:30	0.00	0	Interpolation	2.83
18:30–22:30	0.03	$\geqslant 3$	Log-normalized	1.62
22:30–2:30	0.36	$\geqslant 3$	Log-normalized	5.71
2:30–6:30	0.25	2	Default to period 23	5.71

[a] Times are in Pacific Daylight Savings Time.

Table 4
Emissions fitting methods[a]

	Number of pairs of measured and modeled concentrations both $>0.1\,\mu g\,m^{-3}$	
	$\geqslant 3$ pairs $>0.1\,\mu g\,m^{-3}$	<3 pairs $>0.1\,\mu g\,m^{-3}$
$SE_b > 1.5$	Measured/modeled	Interpolation
$SE_b \leqslant 1.5$	Log-normalized method of least squares	Interpolation

Measured/modeled refers to using the measured/modeled default method which uses the mean of all measured concentrations/mean of all modeled concentrations for the entire set of data, including non-detects (set to $0.1\,\mu g\,m^{-3}$), as a default emission rate when the standard error for the natural log-normalized method of least squares is >1.5 but the number of valid pairs is $\geqslant 3$.

Interpolation refers to using a weighted average default interpolation method to predict the emission rate when other methods are infeasible due to data limitations or the number of valid pairs as explained above is <3 for a dataset of eight monitoring sites or more. In this case, the emission rate is simply the average value, weighted by separation in time from the specific period, of the two nearest non-defaulted values.

[a] Log-normalized refers to the natural log-normalized method of least squares for periods for which the number of valid pairs is $\geqslant 3$ (both measured and modeled concentrations for a receptor must be $>0.1\,\mu g\,m^{-3}$ to be considered a valid pair) and the standard error of the dataset is <1.5.

7. Identification of alternative sealing methods to improve product retention in the soil

Based on review of the two initial field studies conducted in 1999, it was concluded that steps were needed to reduce off-gassing rates and improve the emissions fitting methodology; (1) laboratory research and pilot field studies were needed to identify preferred ways to seal the field; and (2) the design of the air quality monitoring networks were modified to (a) increase the number of monitoring stations from 10–15 or more and (b) reorient the design of the air quality monitoring network to provide more uniform coverage throughout the compass headings (Figs. 3 and 4).

Interpretation of the measured air quality data collected in the baseline studies led to the conclusion

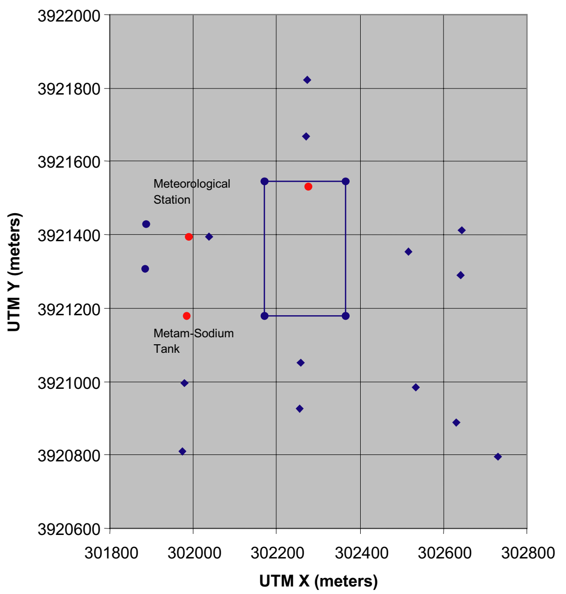

Fig. 3. Site plan for the field and monitoring stations at the Kern 2001 study of intermittent water sealing of a chemigation application. (Merricks, 2002b).

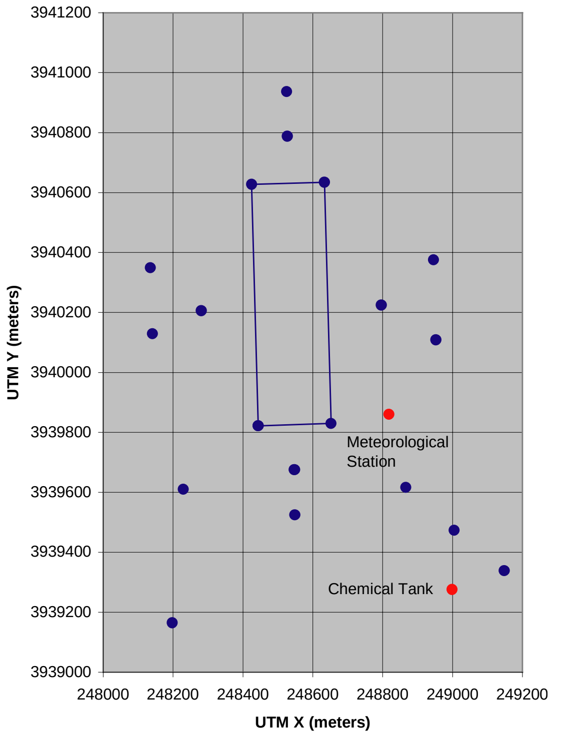

Fig. 4. Lost mills 2000 shank injection field and monitoring stations with intermittent water sealing (Merricks, 2001). Blue dots represent the monitoring stations surrounding the fields (150–800 m).

that alternative application and sealing procedures were needed to provide an option to reduce off-gassing rates, especially during nighttime periods. The emission rates for the baseline studies showed strong diurnal influences, with the nighttime periods producing higher computed emission rates than the daytime periods. This observation is significant in terms of managing exposures downwind of the field because nighttime periods often are associated with relatively low wind speeds and ground-based atmospheric inversion conditions. Such conditions are not conducive to rapid dilution of emissions.

Subsequent to the baseline field studies and initial data interpretation, a laboratory-based sealing research study was conducted to help identify preferred methods to reduce off-gassing for both chemigation and shank injection (Merricks, 2000). This study involved testing relative emission rates for simulation of both major application methods (chemigation and shank injection). Air and soil temperatures in the chambers that were used to conduct these studies were maintained at a constant 90°F, i.e. diurnal temperature cycles were not simulated. Routine sealing methods for chemigation applications in California were simulated as the reference sealing method (typically $\frac{1}{2}$ in of water applied over 2-h periods at the completion of each application, followed by a second seal of $\frac{1}{2}$ in applied 24 h later).

Alternative sealing methods were tested including mechanical compaction, foam, tarp, and a method termed "intermittent water sealing." All tests were conducted with three replicates. The relative results are shown in Fig. 5. As shown, intermittent water sealing and tarps (virtually impermeable film (VIF)) were shown in this research to be the most effective methods to reduce off-gassing rates. The intermittent water sealing for shank injection was clearly shown in this study to provide the potential to increase field retention and reduce off-gassing rates. The results in terms of the benefits of intermittent water sealing for chemigation were mixed. The first trial showed benefits comparable to the shank injection trials. The subsequent two trials did not.

The results of this sealing research were significant in terms of identifying a cost-effective way to reduce off-gassing. While the VIF tarp material showed comparable control benefits to those for intermittent sealing, the labor and material costs involved with VIF tarp are much more expensive than the use of additional water. Prior to conducting major field studies for intermittent water sealing, however, pilot testing was first done to confirm that similar results would be shown in the field when strong diurnal cycles exert an influence on maximum and minimum off-gassing rates throughout the diurnal cycle.

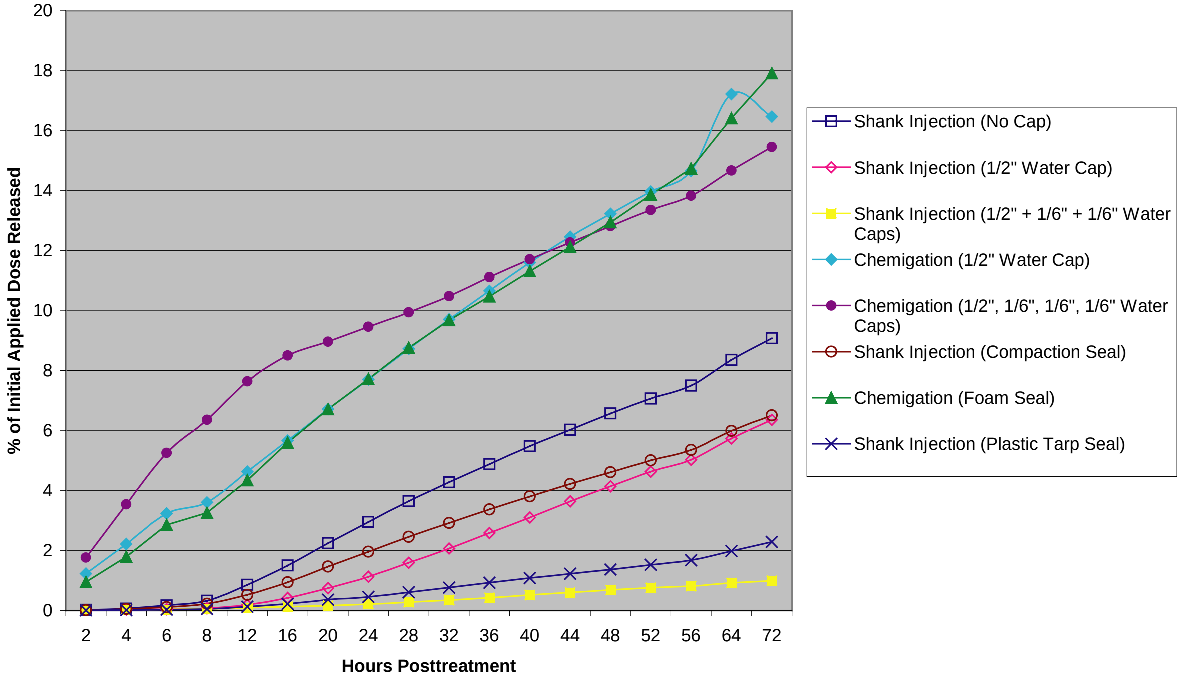

Fig. 5. Laboratory study (Merricks, 2000). Analysis of the cumulative MITC air samples released from the soil by type of application and sealing method (average results based on three replicates each).

8. Pilot-testing of alternative sealing concepts

The pilot studies collected on-site meteorological data at a 3-m height for wind direction and wind speed and at 2 m for ambient temperature. It is expected that the emission rates calculated at the height of the anemometer (3-m) would be less than the emission rates using the standard 10-m height, due to increasing wind speed with height (increasing wind speed would tend to decrease the modeled concentrations, thus increasing the calculated emission rates). Therefore, in order to match the emission rates at the height used in the main field studies, the emission rates were conservatively adjusted. The geometric mean height of the two heights (3–10 m) and the power law formula were used to adjust the wind speeds (Panofsky and Dutton, 1984). On average, wind speeds were increased by 1.1 $\mathrm{m\,s^{-1}}$ under neutral or unstable atmospheric conditions, and increased by 1.3 $\mathrm{m\,s^{-1}}$ under stable atmospheric conditions for the pilot studies.

8.1. Shank injection

A pilot test was conducted in Santa Barbara County, CA in May 2000 (Sullivan et al., 2000b). This test involved two 10-acre plots approximately 800 m apart. Both fields were applied concurrently using two injection rigs. The emission rates calculated in all of the pilot studies were computed by the default approach of multiplying the ratio of mean measured/mean modeled concentrations by the emission rate used in the normalized modeling analysis. This modified approach was deemed necessary because of the small number of data points in the pilot studies (typically 4 monitoring sites per field studied (total of 8 sites)). The results showed emission reduction benefits that are comparable to the laboratory research. Two sealing methods were used in this pilot study (see Table 5). Both sealing methods involved a double seal on the first day; i.e. one immediately following the application and another during the evening hours. Whether applied over a 2-h period near sunset, or during two periods near the period of 6 p.m. to midnight, the extra water applied at night was shown in this study to substantially reduce emissions relative to standard water sealing methods.

8.2. Chemigation

Two pilot studies were conducted for chemigation applications. The first study was performed in Lancaster, CA (Sullivan et al., 2000a). This test involved two 16-acre plots separated by approximately 2.5 km. The results suggest that the application of water seals during the evening, as compared with standard sealing during

Table 5
Water sealing approaches for Santa Barbara study (Sullivan et al., 2000b)

Irrigation set	Intermittent sealed field	Standard seal plus extra $\frac{1}{2}''$ seal on 1st day near sunset
1st	$\frac{1}{2}''$ 11:30 AM–1:30 PM 5/23/00	$\frac{1}{2}''$ 11:30 AM–1:30 PM 5/23/00
2nd	$\frac{1}{6}''$ 7:00–7:30 PM 5/23/00	$\frac{1}{2}''$ 7:00–9:00 PM 5/23/00
3rd	$\frac{1}{6}''$ 10:00–10:30 PM 5/23/00	$\frac{1}{2}''$ 7:00–9:00 PM 5/24/00
4th	$\frac{1}{6}''$ 2:00–2:30 AM 5/24/00	
5th	$\frac{1}{6}''$ 7:00–7:30 PM 5/24/00	
6th	$\frac{1}{6}''$ 10:00–10:30 PM 5/24/00	
7th	$\frac{1}{6}''$ 2:00–2:30 AM 5/25/00	

the afternoon, as with Merricks (1999), produce substantially lower maximum emission rates. It should be noted, however, that the average soil temperature during the Lancaster pilot study was 55°F compared with 80°F for the GLP baseline study for chemigation. Lower soil temperatures would be expected to reduce emission rates. It also should be noted that the Lancaster study did not have an extra water seal immediately after the set. It was concluded after the interpretation of this study that better control could be obtained if the seals were applied immediately upon completion of the application, and then again on an intermittent basis on the evening of the day of application, and once again the following evening.

Another pilot study was conducted in Bakersfield, CA in June 2001 (Sullivan et al., 2001). The intermittent sealing methodology was modified to add an additional sealing period, i.e. an initial water seal of $\frac{1}{2}$in immediately at the conclusion of the application, followed by a $\frac{1}{4}$in seal applied in 1 h starting 1 h before sunset, and a second $\frac{1}{4}$in seal applied over 1 h near midnight. Two $\frac{1}{4}$in seals were applied during the same evening periods of the second day. This adjustment to the sealing procedure showed major reductions in off-gassing rates. A second field was applied with metam-sodium following the first 24-h of the study, delayed for logistical reasons. Due to the close proximity of the two fields (<800 m), some interference from each field likely occurred, increasing the concentration at each monitoring station and thus elevating the emission rates. Data following the first six periods were not used in the comparative emission rate analysis. A major GLP study was conducted in Bakersfield, CA in August 2001 to further confirm the chemigation pilot study results, as described below.

9. GLP field studies of alternative sealing practices

Studies were conducted in the summer of 2000 and 2001 to provide a more robust data set to identify the reduction in emission rates that could be achieved using intermittent water sealing. The studies employed the same ambient monitoring and modeling analyses as previously described for Merricks (2002a) (96-h monitoring period with 24, 4-h samples taken), except that 15 station monitoring networks were established instead of 10 station networks. Tables 6 and 7 show the estimate of emission rates and the method employed to determine them for the intermittent sealed studies. Figs. 6 and 7 summarize the emission rates for the baseline and intermittent water sealing methods for chemigation and shank injection, respectively. The results in both cases showed major reductions in off-gassing losses of MITC, as well as a dramatic drop in emission rates during the critical nighttime period, when intermittent sealing was used.

10. Results and discussion

As a demonstration of the emissions rate methodology, an example of a comparison of the measured and modeled MITC concentrations for all monitoring stations multiplied by the estimated emission rate for sampling period 10 of the intermittent seal chemigation study (Merricks, 2002a, b) is provided in Fig. 8. Fig. 9 shows a graph of the field and the measured concentration at the monitors compared with the estimated plume using the modeled concentrations and the estimated of emission rate for that period (period 10 was selected for the large number of measured and modeled non-zero pairs and the typical standard error of the estimate found throughout the periods). This figure shows an example of how model-computed MITC concentrations compared with the measured MITC concentrations at the monitoring stations. The measured data do not exactly match the modeled data multiplied by the estimated emission rate for all monitoring stations. The estimate of the emission rate has some uncertainty associated with it; however, the description of that uncertainty is beyond the scope of this paper. In a companion paper, a modeling system is described that

Table 6
Lost hills shank injection intermittent seal study (Merricks, 2001)[a]

Period	Standard error	Valid pairs	Emissions calculation method used	Final emission rate
7:00–11:00	**1.69**	⩾3	Measured/modeled	14.17
11:00–15:00	1.34	⩾3	Log-normalized	16.85
15:00–19:00	0.91	2	Interpolation	14.01
19:00–23:00	0.47	⩾3	Log-normalized	11.18
23:00–3:00	0.19	⩾3	Log-normalized	4.09
3:00–7:00	0.13	2	Interpolation	3.27
7:00–11:00	0.28	⩾3	Log-normalized	2.45
11:00–15:00	0.32	⩾3	Log-normalized	15.47
15:00–19:00	0.32	⩾3	Log-normalized	22.81
19:00–23:00	0.38	⩾3	Log-normalized	8.07
23:00–3:00	0.20	⩾3	Log-normalized	2.21
3:00–7:00	0.04	⩾3	Log-normalized	4.15
7:00–11:00	0.12	⩾3	Log-normalized	1.89
11:00–15:00	0.25	2	Interpolation	3.25
15:00–19:00	0.09	⩾3	Log-normalized	4.62
19:00–23:00	0.11	⩾3	Log-normalized	3.44
23:00–3:00	0.15	⩾3	Log-normalized	1.90
3:00–7:00	0.05	⩾3	Log-normalized	1.72
7:00–11:00	0.06	1	Default to period 13	1.89
11:00–15:00	0.00	0	Default to period 14	3.25
15:00–19:00	0.00	0	Default to period 15	4.62
19:00–23:00	0.07	2	Default to period 16	3.44
23:00–3:00	0.08	1	Default to period 17	1.90
3:00–7:00	0.00	0	Default to period 18	1.72

[a] Times are in Pacific Daylight Time.

Table 7
Kern 2001 chemigation intermittent seal study (Merricks, 2002b)[a]

Period	Standard error	Valid pairs	Method	Final emission rate
5:00–9.00	0.45	⩾3	Log-normalized	9.28
9.00–13:00	0.19	⩾3	Log-normalized	7.45
13:00–17:00	1.15	⩾3	Log-normalized	92.80
17:00–21:00	0.89	⩾3	Log-normalized	18.36
21:00–1:00	0.46	⩾3	Log-normalized	5.84
1:00–5:00	0.53	⩾3	Log-normalized	3.77
5:00–9.00	0.31	⩾3	Log-normalized	5.38
9.00–13:00	0.13	⩾3	Log-normalized	3.47
13:00–17:00	0.85	⩾3	Log-normalized	72.78
17:00–21:00	0.46	⩾3	Log-normalized	18.72
21:00–1:00	0.46	⩾3	Log-normalized	3.84
1:00–5:00	0.12	⩾3	Log-normalized	3.05
5:00–9.00	0.13	⩾3	Log-normalized	2.77
9.00–13:00	0.27	⩾3	Log-normalized	1.77
13:00–17:00	0.32	⩾3	Log-normalized	13.43
17:00–21:00	0.36	⩾3	Log-normalized	25.39
21:00–1:00	0.44	⩾3	Log-normalized	5.73
1:00–5:00	0.29	⩾3	Log-normalized	4.96
5:00–9.00	0.43	⩾3	Log-normalized	1.95
9.00–13:00	0.21	⩾3	Log-normalized	2.25
13:00–17:00	0.38	⩾3	Log-normalized	4.33
17:00–21:00	0.57	⩾3	Log-normalized	9.17
21:00–1:00	0.25	⩾3	Log-normalized	6.12
1:00–5:00	0.45		Log-normalized	3.13

[a] Times are in Pacific Daylight Savings Time.

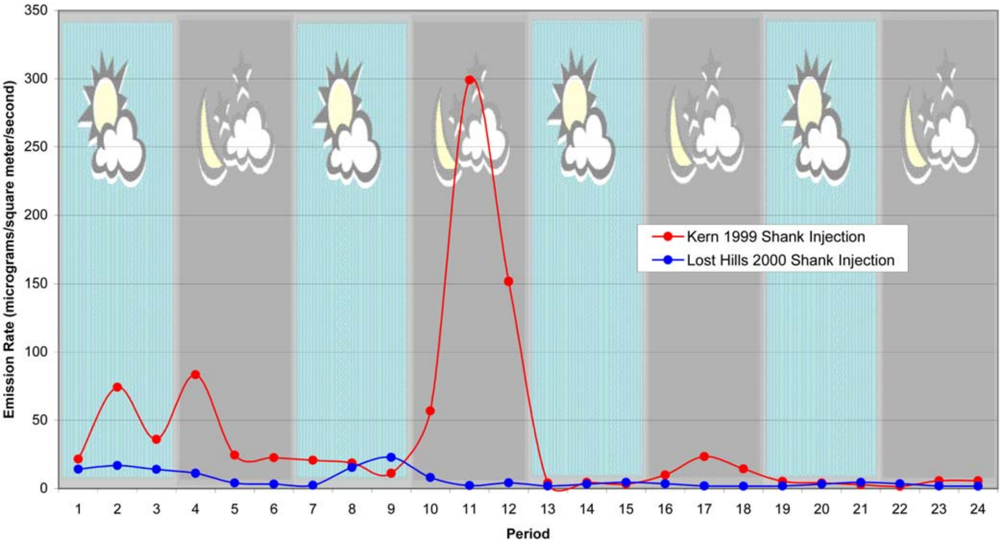

Fig. 6. Comparison of the median off-gassing rates for the MSTF GLP shank injection studies (1999–2000).

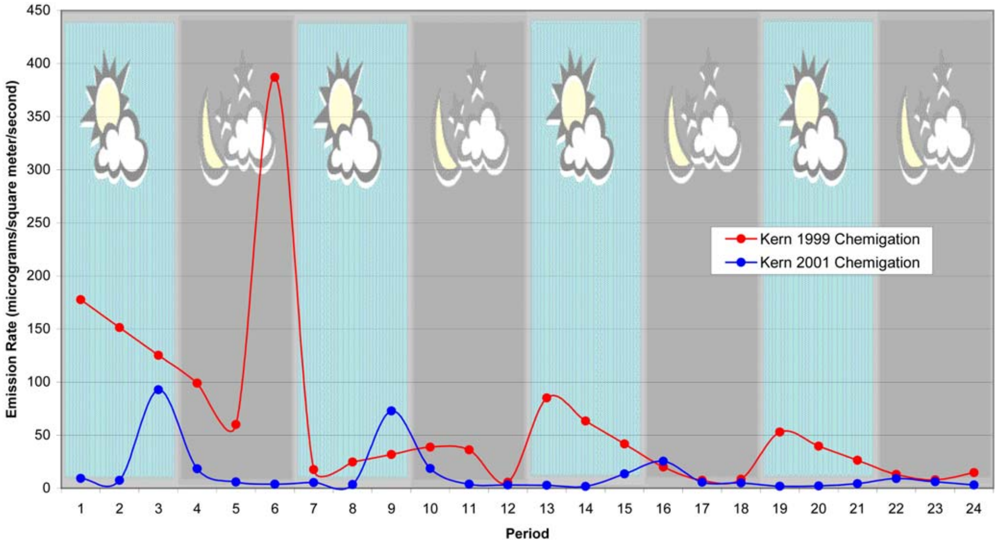

Fig. 7. Comparison of the median off-gassing rates for the MSTF GLP Chemigation studies (1999–2000).

accounts for this uncertainty (*Monte Carlo-based dispersion modeling of off-gassing releases from the fumigant metam-sodium for determining distances to exposure endpoints*).

The revised monitoring network design incorporated into the GLP field studies in 2000 and 2001 reduced the number of 4-h periods that required default methods to estimate emission rates. Lost Hills had four defaults for periods 1–18, which included all periods with measured concentrations above general background levels. Periods 19–24 (the last six) were all defaulted because of low concentrations (near the detection limit). Emission rates could not be accurately calculated for these periods. Kern (2001) had no defaults for any of the 24 periods. The larger number of sampling sites (15) and more uniform coverage was more effective in consistently tracking emissions. Another factor that enhances the fitting procedure is the variability of wind direction over each 4-h period that is evaluated. A greater degree of

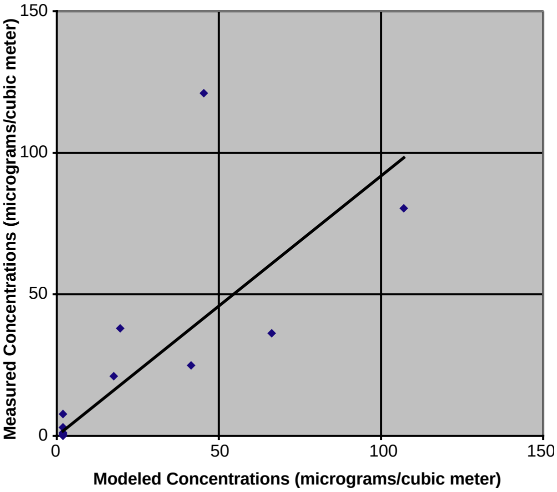

Fig. 8. Comparison of the natural log-normalized modeled concentrations vs. measured MITC concentrations for period 10 of the Kern 2001 Chemigation intermittent Seal GLP field study (Merricks, 2002b).

variability in wind direction increases the number of samples to fit the emission rates.[2]

Intermittent water sealing is effective for metam-sodium applications because of the solubility of MITC in water (7600 mg l^{-1} at 20° C) relative to the other methyl bromide alternatives (Yalkowsky and Dannenfelser, 1992). The timing of the application and the timing of the water seals were both found to be important. By starting the application shortly after sunrise, and completing the application by noontime to 1:00 p.m., it is possible to apply a 2-h water seal to contain MITC in the treatment zone during the hot afternoon period. Returning to apply additional water seals near sunset, and again near midnight, adds to the water reservoir as the ground-level inversion is beginning to set up. Applying water seals in this manner provides the following benefits in terms of reducing emission rates: (a) increases the water reservoir to contain the MITC in the liquid phase and minimizes volatilization losses; (b) decreases the air porosity in the soil; (c) moves the liquid-phase MITC further down into the treatment zone (subsequent to at least 6 h following application to allow for a strong dose in the treatment zone) and away from the surface where volatilization losses occur; and (d) increases the heat capacity and heat conductivity of the soil.[3]

As a related issue, the initial soil moisture is expected to be important to the success of the intermittent water sealing method. The baseline chemigation study (Merricks, 2002a) had lower initial moisture, in terms of percent field capacity, relative to the Kern 2001 study of intermittent water sealing for chemigation (see Table 8). The baseline shank injection study using standard water sealing had more initial moisture than the intermittent shank injection study in terms of percent field capacity, although the total volumetric moisture was lower.

11. Summary and conclusions

Based on the field studies conducted to date, the use of intermittent water sealing, has been shown to be effective in improving field retention of MITC and reducing off-gassing rates of MITC from metam-sodium applications. One of the most important benefits of the intermittent sealing method is the order(s) of magnitude reduction in maximum emission rates at night. As fumigants are being reviewed in greater detail in terms of exposures to individuals downwind of the field, the ability to minimize off-gassing rates during nighttime periods with the potential for worst-case meteorological conditions likely will become of even greater importance.

Aside from the environmental and health and safety benefits of reducing off-gassing emissions from fumigants used for agricultural purposes, the potential benefits in terms of dose enhancement within the treatment zone also may be beneficial in terms of biological efficacy. Resources allocated towards minimizing off-gassing results can lead to greater retention of liquid-phase MITC or other fumigants in the treatment zone. Because the biocidal properties of MITC are primarily delivered in the liquid phase, this factor is especially significant. Growers can more efficiently and cost-effectively use metam-sodium at the same time they are improving environmental management.

The results shown in this study need to be extrapolated with caution to other soil types and conditions. Different water usage rates and different benefits can be anticipated for different soils and environmental conditions. It also should be noted that alternative sealing methods would be needed if sufficient water is not available to support the intermittent sealing method described in this paper.

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[2] Increasing the averaging time and the number of monitoring sites will more broadly cover the plume and increase the number of valid pairs of measured and modeled data. Six-hour averaging blocks will be evaluated in future studies to seek optimal conditions to distribute the plume among the different sites in the sampling network while minimizing the potential to cross diurnal cycles, e.g. 7:30–13:30, 13:30–19:30, 19:30–1:30, and 1:30–7:30.

[3] The soils in these studies were generally sandy loam or in some cases, clay loam soil. Especially for the sandy soil, heat capacity is relatively low, which may lead to convective losses from the soil during ground-based atmospheric inversion conditions. By applying more water, and on an intermittent basis, the heat capacity is increased and the potential for convective losses is reduced.

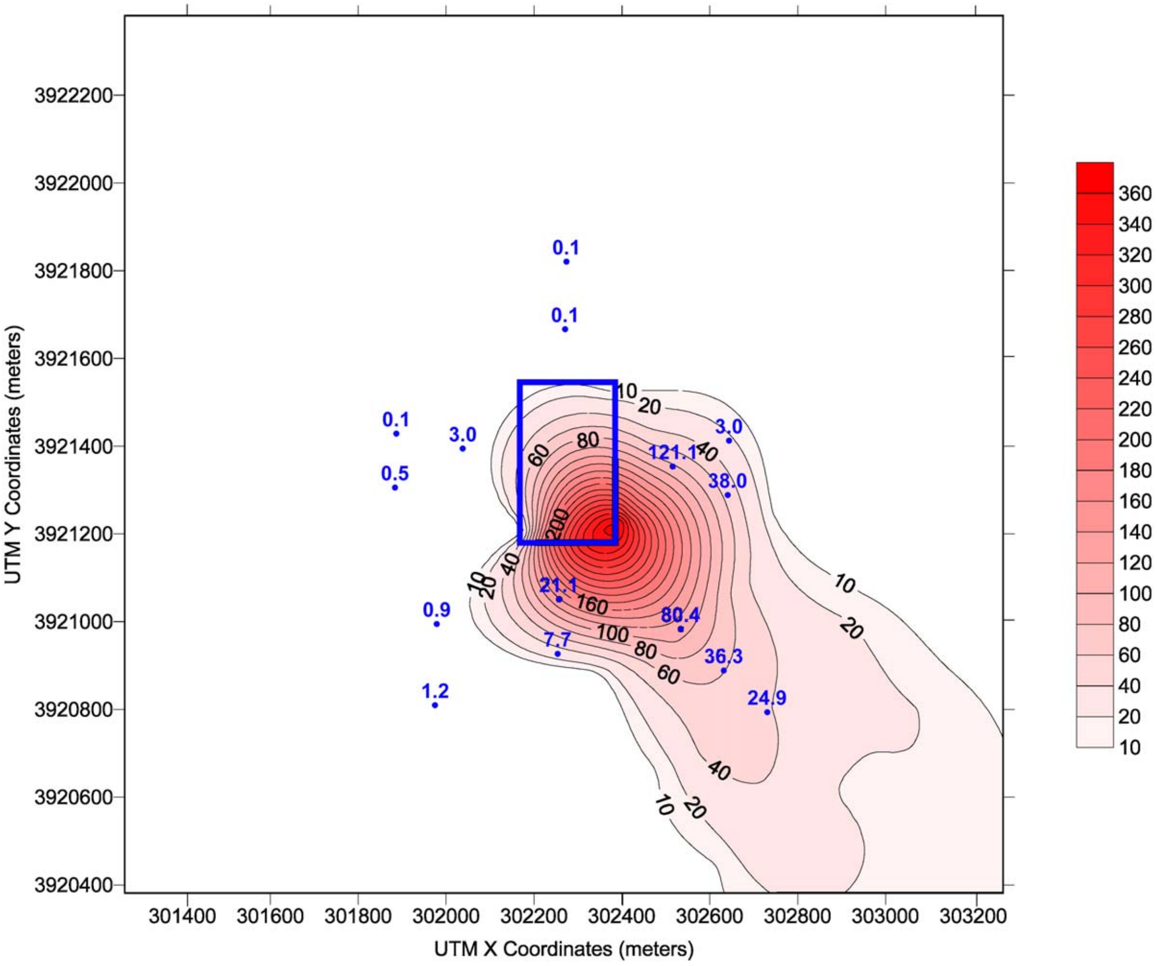

Fig. 9. Analysis of period 10 of the Kern 2001 intermittent seal GLP study (Merricks, 2002b) MITC modeled concentration isopleths (micrograms/cubic meter) using an emission rate of $18.7\,\mu g\,m^{-2}\,s^{-1}$ compared with the measured MITC concentrations at each Monitoring Station (indicated by the blue dots).

Table 8
Soil moisture

Field study	Soil type	% Field capacity	% Initial volumetric soil moisture
Kern, 1999 shank, injection[a]	Sandy loam	68	9
Kern, 1999 chemigation[a]	Sandy loam	29	3
Lost hills, 2000 shank, injection[b]	Clay loam	54	12
Kern 2001, chemigation[c]	Silt loam	60	6

[a] Merricks (2002a).
[b] Merricks (2001).
[c] Merricks (2002b).

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