

## Determination of Methyl Isothiocyanate in Air Downwind of Fields Treated with Metam-Sodium by Subsurface Drip Irrigation

JAMES E. WOODROW,<sup>\*,†</sup> JAMES N. SEIBER,<sup>‡</sup> JAMES S. LENOIR,<sup>†</sup> AND  
 ROBERT I. KRIEGER<sup>§</sup>

Natural Resources and Environmental Science, University of Nevada, Reno, Nevada 89557; USDA-ARS, Albany, California 94710; and Personal Chemical Exposure Program, Department of Entomology, University of California, Riverside, California 92521

Air concentrations of methyl isothiocyanate (MITC) were determined near two fields treated with metam-sodium (MS) by subsurface drip irrigation. The two study fields showed measurable airborne MITC residues during application of MS and for periods up to 48 h postapplication. Using a Gaussian plume dispersion model, flux values were estimated for all of the sampling periods. On the basis of the flux estimates, the amount of MITC that volatilized within the 48 h period was about 1.4% of the applied material. Compared to other studies, MITC residues in air measured during application by subsurface drip irrigation were up to four orders-of-magnitude lower than those previously published for applications involving delivery through surface irrigation water. Our measured concentrations of MITC in field air were at levels below current regulatory guidance and thresholds for adverse human health effects.

**KEYWORDS:** Metam-sodium; MITC; atmosphere; vapor sampling; exposure

### INTRODUCTION

Metam-sodium (MS:  $\text{CH}_3\text{NHCS}_2\text{Na}$ ) is used in agriculture as a soil fumigant to control weeds, nematodes, fungi, and soil insects. When diluted in water, and especially in basic media and in the presence of heavy metal salts, MS decomposes into methyl isothiocyanate (MITC:  $\text{CH}_3\text{N}=\text{C}=\text{S}$ ), which is the chemical that actually accomplishes the soil fumigation (1–3). MITC is volatile (vapor pressure: 2.5–2.8 kPa at 20 °C (4, 5); Henry's constant:  $\sim 10 \text{ Pa}\cdot\text{m}^3/\text{mole}$  (6)), and some will therefore diffuse out of the soil into the atmosphere over treated fields (7), where it can move into nontarget areas by diffusion and advection.

MITC is one of several soil fumigants commonly used to control soil pests and plant pathogenic microbes. Until recently, methyl bromide (MeBr) was the most widely used fumigant because of its broad-spectrum efficacy. But, the fact that this fumigant is a class I ozone-depleting chemical has led to a proposed reduction in usage and an eventual phase-out (8, 9). The remaining widely used registered fumigants (e.g., chloropicrin, 1,3-D, and MS) have increased in usage, singly and in various combinations (e.g., MS with chloropicrin) as replacements for MeBr. MITC has a definite environmental advantage

over MeBr in that MITC is much less stable in the troposphere (half-life  $\approx 33 \text{ h}$ , compared to  $\sim 0.7$  years for MeBr), where it will readily undergo light-catalyzed conversions (10, 11). Because of this and its chemical makeup, MITC is not considered to be an ozone-depleting chemical.

Emissions during and after application represent a pathway for losses of MITC to the atmosphere and subsequent movement to nontarget areas. Because of this, there is concern over possible risks from exposure to this fumigant that might have acute or chronic human health or ecological impacts. As a result, there is an increasing demand for concentration data in air for assessment of exposure and risk. Important goals of this study include the determination of air concentrations of MITC adjacent to and downwind from two fields treated with MS by injection into the subsurface drip irrigation system and estimations of MITC evaporative flux for each sampling period. The results serve as a basis for estimating the downwind airborne exposure to MITC from this method of application.

An important aspect of this study was a comparison of the various common methods for MS application. Application method evaluations were made based on the magnitude of downwind concentrations and evaporative flux of MITC. Emission reduction becomes important when considering buffer zone restrictions, which are already in place in California for MeBr and are proposed for MITC (12). The U.S. EPA has imposed buffer zone restrictions on the newly registered methyl iodide fumigant, and it may soon require restrictions for other fumigants as well (13).

\* To whom correspondence should be addressed. E-mail: jwoodrow@unr.nevada.edu.

<sup>†</sup> University of Nevada.

<sup>‡</sup> USDA-ARS.

<sup>§</sup> University of California.

## MATERIALS AND METHODS

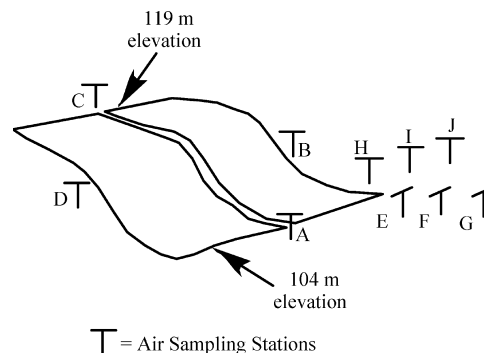
**Laboratory.** A widely used method for trapping MITC from air is to perform cumulative sampling through charcoal tubes, followed by solvent elution and gas chromatographic determination using flame ionization or nitrogen–phosphorus detectors (1, 14–17). An alternative analytical method involves benzyl alcohol elution of charcoal in a sealed vial to release the MITC, followed by headspace gas chromatography (18).

In general, we adopted the approach of cumulative sampling through charcoal tubes, followed by elution of the trapped material from charcoal using an organic solvent, and determination of the amount of MITC in the solvent extract using gas chromatography with nitrogen–phosphorus thermionic detection of the liquid injections. Specifically, duplicate spikes of 100 and 400 ng of MITC were made into the intakes of air sampling tubes containing 1 g of coconut charcoal (SKC West, Fullerton, CA) by depositing the spikes, while air was flowing at about 2 L/min, onto small polyurethane foam (PUF) plugs inserted into the tube intakes. Airflow was maintained for about 4 h using battery-powered pumps (PCXR8 Universal Sampler; SKC West). Air blanks (i.e., no MITC spikes) were also run at the same time.

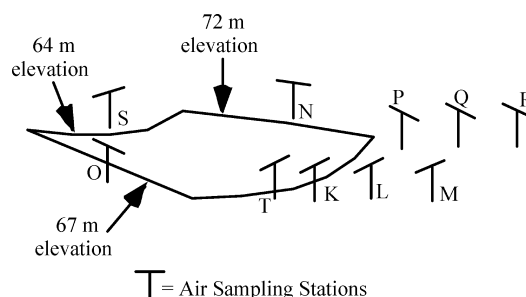
At the end of the sampling period, the spiked PUF plugs and tube contents were placed in separate 20 mL glass vials; 5 mL of desorbing solvent (50:50 v/v ethyl acetate/carbon disulfide) was added to each vial, and the vials were sealed with Teflon-lined screw caps. The sealed samples were sonicated at low intensity for about 1 min. The extract was then filtered through a 0.45  $\mu\text{m}$  Teflon-membrane filter into 2 mL autosampler vials. By using a model 7673 autoinjector (Agilent, San Fernando, CA), 4  $\mu\text{L}$  of each sample was injected onto a 30 m  $\times$  0.53 mm (id) DB-1701 fused silica open tubular (FSOT) column (J&W Scientific, Folsom, CA) and determined using an H–P 5890 series II gas chromatograph equipped with a nitrogen–phosphorus thermionic detector (Agilent). Specifically, the FSOT column was held at 80  $^{\circ}\text{C}$  for 1 min, after which time it was heated at a rate of 10  $^{\circ}\text{C}/\text{min}$  to 105  $^{\circ}\text{C}$  (no hold). The carrier gas (helium) flow rate was set at about 4 mL/min, which gave an approximate retention time for MITC of about 2.3 min under the oven temperature program stated above. Air blanks and reagent blanks were also processed at the same time. Standard curves were based on injections of pure MITC dissolved in the binary solvent.

**Field Monitoring.** The method described above was applied to two field sampling situations. The fields (field 1: 4 ha; field 2: 1.2 ha), located on Murai Farms in Orange County, California, were commercially treated with MS by subsurface drip irrigation. Both fields were treated with 700 L/ha Vapam HL (0.5 kg/L MS; ZENECA, Inc., Ag Products, Wilmington, DE) injected at a depth of about 10 cm. Treatment of field 1, which was untarped, began at about 1800 h mid February 1997 and was completed 4 h later. Treatment of field 2, with only the planting rows tarped with 1.5 mm thick plastic mulch, began at about 1820 h late March 1997 and was completed 2.4 h later.

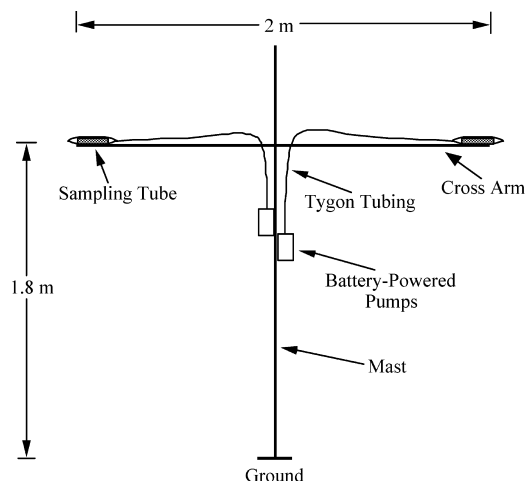
Prior to each application, wind speed and direction data were collected overnight during a 12 h period, and the data were then analyzed to help determine the best sampling mast distribution for two downwind directions. The air sampling masts were then set up around the fields and along two directions downwind of the fields, giving a total of 10 masts per field (Figures 1 and 2). Each sampling mast consisted of a cross-arm at 1.8 m height that held two charcoal sampling tubes at opposite ends of the cross-arm and two battery-powered pumps (Figure 3). The pump flows were set at 2 L/min, but the actual flow was measured at the start and end of each sampling period using calibrated rotameters (Gilmont, no. 3203–20; Barnant Co., Barrington, IL). The sampling masts and meteorological equipment (Campbell Scientific, Logan, UT) were operated prior to application, during application, and during a number of 4 h sampling periods up to 48 h postapplication. At the end of each sampling period, the charcoal tubes were capped and placed in plastic bags with labels indicating the sampling periods. The bags were stored on dry ice for transport to the University of Nevada, Reno, where the samples were stored at  $-20^{\circ}\text{C}$  prior to analysis. Two sets of three clean, unused charcoal tubes each were spiked with 10  $\mu\text{L}$  of 0.20  $\mu\text{g}/\mu\text{L}$  and 2.0  $\mu\text{g}/\mu\text{L}$  MITC standard, respectively, and stored in the freezer along with the field samples to determine storage stability. All samples were assayed using the method described above.



**Figure 1.** Air sampling stations A–J distributed around field 1 (not tarped). Distances to sampling stations from the nearest edge of the field are as follows: A, 3 m; B, 4 m; C, 4 m; D, 4 m; E, 6 m; F, 15 m; G, 43 m; H, 8 m; I, 15 m; J, 50 m.



**Figure 2.** Air sampling stations K–T distributed around field 2 (tarped). Distances to sampling stations from the nearest edge of the field are as follows: K, 6 m; L, 15 m; M, 50 m; N, 3 m; O, 3 m; P, 6 m; Q, 15 m; R, 50 m; S, 4 m; T, 4 m.



**Figure 3.** Configuration of the MITC sampling towers.

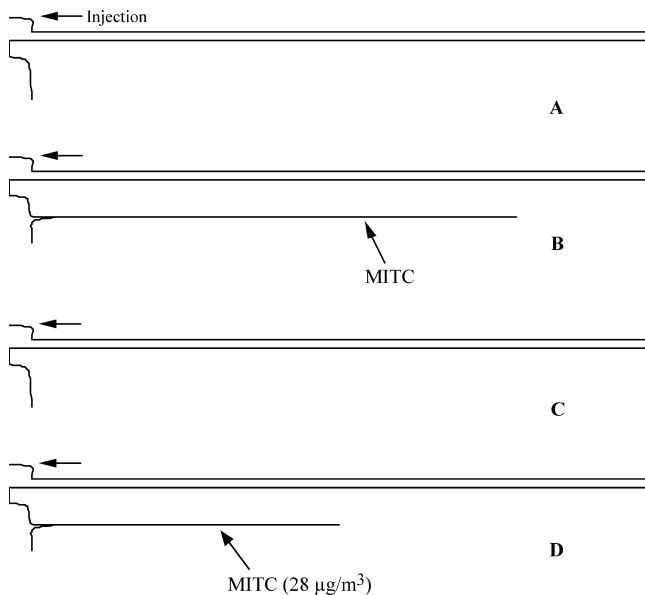
**Field Modeling.** Evaporative flux for each sampling period was estimated by back-calculation using the U.S. EPA ISCST3 Gaussian plume dispersion model (19). Five-minute averaged meteorological data measured at the fields were used in the model, along with mixing height and stability class estimates obtained from other sources. The model was run under the gradual plume rise and no buoyancy-induced dispersion conditions in a rural setting. Default wind profile exponents and vertical temperature gradients were used, and the complex terrain option was selected. For each sampling period, the model was initially run with an arbitrary flux value,  $f$ , and the observed air concentrations and ISCST3-predicted concentrations were regressed, with the model-predicted concentrations as the abscissa. To estimate the actual flux, the slope of the regression line was multiplied by  $f$  (20).

For comparison, evaporative flux was also estimated using correlation techniques described elsewhere (21, 22). A comparison of the physicochemical properties and application conditions of MITC was made

**Table 1.** Recovery of MITC from Charcoal and Air Spikes

amount spiked (ng)	sampling time (h)	amount recovered (ng)	% recovered
100	0 <sup>a</sup>	80.9 ± 0.1	80.9 ± 0.1
400	0 <sup>a</sup>	323 ± 17	80.7 ± 4.0
100	4 <sup>b</sup>	79.0 ± 3.5	79.0 ± 3.5
400	4 <sup>b</sup>	320 ± 16	80.0 ± 4.0

<sup>a</sup> Spiked directly to charcoal. <sup>b</sup> 2 L/min air flow.

**Figure 4.** Gas chromatograms of a charcoal blank (A), MITC standard (B), field air blank (C), and field sample (D).

with the properties and conditions of another common fumigant, methyl bromide. Given water solubility ( $S_w$ ), soil adsorption coefficient ( $K_{oc}$ ), vapor pressure (VP), application rate (AR), and depth of application ( $d$ ), the following operation was made to estimate emission rate for MITC:

$$(R[\text{MITC}]/R[\text{MeBr}]) \times \text{ER}(\text{MeBr})$$

where  $R = (VP \times AR)/(S_w \times K_{oc} \times d)$  and ER is the measured emission rate for methyl bromide. In the above relationship,  $R(\text{MITC}) = 0.0888$ ,  $R(\text{MeBr}) = 1.734$ , and  $\text{ER}(\text{MeBr}) = 83.5 \mu\text{g}/(\text{m}^2 \cdot \text{s})$  (measured range: 76–91  $\mu\text{g}/(\text{m}^2 \cdot \text{s})$  (23, 24)).

## RESULTS

**Laboratory.** Table 1 summarizes the air sampling recovery data for the MITC spikes. Recovery from charcoal (~80%) was essentially the same for residues spiked directly to the charcoal as for residues trapped as vapor from air. On the basis of the data in Table 1, trapping efficiencies (ratios of recovery from spiked air to recovery from spiked charcoal) for 100 and 400 ng spikes to air were 97.6 and 99.1%, respectively, for 4 h of sampling at 2 L/min flow.

Freezer spikes, which were removed after about a 2–3 month storage, had an overall MITC recovery of  $79.4 \pm 10.8\%$ . Since recovery from spiked charcoal was about 80%, these results indicate that MITC was stable on charcoal at freezer temperatures for the duration of the storage period (freezer spike recovery was about 98%, adjusted for recovery from spiked charcoal (Table 1)).

Figure 4 shows typical chromatograms for a charcoal blank, standard spike, field background, and field sample with a response equivalent to  $28 \mu\text{g}/\text{m}^3$  MITC in air. There were no observable peaks from air background at or near the retention

time for MITC. By using three times the standard deviation of the lowest standard and the linear regression fit for a series of standard injections, the limit of quantitation under an airflow rate of 2 L/min was determined to be about  $80 \text{ ng}/\text{m}^3$ . However, typical flow rate for the samplers in the field was approximately 1.5 L/min. Thus, the limit of quantitation was about  $100 \text{ ng}/\text{m}^3$ .

**Field Monitoring.** Ranges of air concentrations around both treated fields for all of the sampling stations over the 48 h duration of the study are summarized in Table 2, along with integrated 48 h average concentrations. Field 1 was characterized by very hilly terrain, which gave rise to some air turbulence that probably contributed to “upwind” MITC residues (Figure 1). For example, measurable MITC residues occurred at station C for all of the sampling periods, but some of these periods were characterized by the station being “upwind” of the field. Field 2 was characterized by smoother, slightly sloping terrain that reduced the potential for turbulence (Figure 2). The smoother terrain apparently did not give rise to the type of air turbulence seen with field 1; so, for the sampling periods during which the wind moved from station O toward the field, this station did not have any observable MITC residues (<LOQ (Table 2)). The measured residues could be explained in terms of some air movement from the field toward station O.

**Field Modeling.** The evaporative flux values estimated for each sampling period using the ISCST3 model are listed in Table 3. A value for period 4, field 1, was not included due to missing meteorological data. Evaporative flux estimated for the application period using correlation techniques was also included for comparison.

## DISCUSSION

**Laboratory.** At about 80%, MITC recovery from charcoal was essentially quantitative. This was fairly consistent, with only about a 5% coefficient of variation at most. Such a recovery was made possible to a large extent by the use of carbon disulfide as part of the eluting solvent. Eluting with pure ethyl acetate resulted in about a 50%, or less, recovery from charcoal. On the other hand, pure carbon disulfide presented a chromatography problem in that the rather large positive response of the nitrogen–phosphorus detector masked the MITC signal. By mixing this solvent with ethyl acetate, the gas chromatographic response of carbon disulfide was attenuated, and the signal recovered quickly back to the baseline well in advance of the MITC signal (Figure 4).

**Field Monitoring.** While charcoal is a reasonable choice as an air sampling medium for MITC in that it efficiently trapped and released the compound using our field and laboratory procedures, there may be some question concerning the stability of MITC on this adsorbent. Charcoal is also a very good adsorbent for water. Under relatively moist conditions (i.e., fog, rain, high humidity) charcoal can adsorb enough water to decrease analyte trapping efficiency and create an alkaline environment (pH > 10) (25, 26). Under mild alkaline conditions (pH = 9), MITC will undergo hydrolysis with a corresponding half-life of about 110 h at 25 °C (5). Fortunately for field 1, relatively warm and clear conditions, characterized by temperature and relative humidity values in the range 10–27 °C (avg: 18 °C) and 12–58% (avg: 28%), respectively, prevailed both day and night during field air monitoring. So, we would not expect that the charcoal sampling tubes adsorbed significant moisture to cause any stability or trapping problems with MITC during the time scale of our sampling periods for field 1. While the temperature range for field 2 was similar to that for field 1,

**Table 2.** MITC Concentration Ranges and Integrated 48 h Concentrations for the Sampling Stations from Fields 1 and 2

field 1 (not tarped)	downwind distance (m)	conc range ( $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>	integrated conc ( $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>	field 2 (tarped)	downwind distance (m)	conc range ( $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>	integrated conc ( $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>
A	3	9–70	24	N	3	2–21	9
B	4	14–34	20	O	3	<LOQ <sup>b</sup> –5	1
C	4	2–17	6	S	4	<LOQ <sup>b</sup> –36	12
D	4	5–44	16	T	4	3–47	18
E	6	11–89	45	K	6	3–51	21
F	15	10–88	41	L	15	2–84	19
G	43	7–56	30	M	50	<LOQ <sup>b</sup> –22	5
H	8	7–58	19	P	6	6–76	18
I	15	3–49	24	Q	15	5–87	18
J	50	0.3–28	16	R	50	3–114	15

<sup>a</sup> Over the 48 h of the study (6, 4 h sampling periods: application and at 4, 8, 24, 36, and 48 h postapplication). <sup>b</sup> LOQ = limit of quantitation ( $\sim 100 \text{ ng}/\text{m}^3$ ).

**Table 3.** Evaporative Flux Values for MITC Estimated Using the ISCST3 Model and Correlation Techniques

field 1 (4 ha)		field 2 (1.2 ha)		correlation
period	flux ( $\mu\text{g}/(\text{m}^2 \cdot \text{s})$ )	period	flux ( $\mu\text{g}/(\text{m}^2 \cdot \text{s})$ )	flux ( $\mu\text{g}/(\text{m}^2 \cdot \text{s})$ )
A <sup>a</sup>	3.12	A <sup>a</sup>	5.00	4.28
4	<sup>b</sup>	4	4.00	<sup>c</sup>
8	2.20	8	2.50	<sup>c</sup>
24	0.81	24	1.00	<sup>c</sup>
36	0.33	36	0.70	<sup>c</sup>
48	0.31	48	0.70	<sup>c</sup>

<sup>a</sup> A = application. <sup>b</sup> Missing data. <sup>c</sup> Not determined.

12–21 °C (avg: 16 °C), the relative humidity was somewhat greater, 52–90% (avg: 76%). This was due primarily to overcast conditions and early morning fog that did not exist for field 1. Other investigators have demonstrated that, within a two-hour period, as much as 38% (wt/wt) moisture will be accumulated by charcoal from water-saturated air at a flow rate of 200 mL/min (25). The high moisture content affected both the stability and trapping efficiency of methyl bromide, a soil fumigant that has similar base-catalyzed hydrolysis rates as those for MITC at elevated pH. However, even with a half-life of 110 h (25 °C), the expected relative recovery for MITC from wet charcoal after a four-hour sampling period would be close to 98%, well within experimental error. The recovery would be even greater if the lower field temperatures are taken into consideration. We did not determine the possible effect of moisture on the trapping efficiency of charcoal for MITC. However, one study has shown that high relative humidity (>90% (20 °C)) caused about 18% of the total methyl bromide recovered from a charcoal sampling train to break through the first tube during sampling (26). At about 40% relative humidity (20 °C), no breakthrough of methyl bromide was observed.

The two study fields gave rise to airborne MITC residues almost immediately upon application of the parent MS and for periods up to 48 h postapplication. Measurable MITC residues were found at all of the sampling stations, up to 50 m downwind. The integrated 48 h MITC levels in the air (1–45  $\mu\text{g}/\text{m}^3$  for all sampling stations) were up to 2 orders-of-magnitude greater than the limit of quantitation ( $\sim 100 \text{ ng}/\text{m}^3$ ). The integrated 48 h concentrations for the stations immediately around each field (i.e., A, B, C, and D (field 1); N, O, S, and T (field 2)) (Table 2) showed the ranges 6–24  $\mu\text{g}/\text{m}^3$  (avg: 16  $\mu\text{g}/\text{m}^3$ ) for field 1 and 1–18  $\mu\text{g}/\text{m}^3$  (avg: 10  $\mu\text{g}/\text{m}^3$ ) for field 2. The integrated 48 h results for the stations at varying downwind distances were 16–45  $\mu\text{g}/\text{m}^3$  (avg: 29  $\mu\text{g}/\text{m}^3$  (field 1)) and 5–21  $\mu\text{g}/\text{m}^3$  (avg: 16  $\mu\text{g}/\text{m}^3$  (field 2)). These comparisons suggest a trend toward lower MITC concentrations for the partially tarped field 2. But, this was probably due as much to difference in field sizes (field 2 = 0.3 × field 1) as to partial tarping. Furthermore, the

differences in terrain, leading to wind patterns unique to each field, would also have a significant but different effect on the relative downwind concentrations for the two fields (27). Therefore, the many independent variables, such as differences in application methodology, terrain, time of year, and meteorology, do not allow a definitive determination of the potential impact of partial tarping on MITC off-site movement. While there was a trend toward lower airborne residues with the partially tarped field, statistically the two fields were essentially equivalent in terms of relative losses of MITC to the atmosphere.

Compared to other studies, the concentrations around fields 1 and 2, resulting from subsurface drip irrigation, were 1–4 orders-of-magnitude lower than those associated with applications involving surface chemigation (28). For example, measured concentrations from our study during application fell in the range 0.3–114  $\mu\text{g}/\text{m}^3$  (avg: 34  $\mu\text{g}/\text{m}^3$ ), while, during application, concentrations from a sprinkler chemigation MS study in California fell in the range 4000–7000  $\mu\text{g}/\text{m}^3$  for downwind distances of 5–150 m (16). In a similar study in Washington state, where MITC in air was measured near the edge of a center-pivot field treated by overhead sprinkler irrigation, concentrations were >800  $\mu\text{g}/\text{m}^3$  near the downwind edge (29). The significantly higher near-field concentrations for surface chemigation suggest that concentrations more remote from treatment sites might be significant. For example, a community air assessment study in Washington state showed that MITC concentrations in residential areas reached a maximum of 67  $\mu\text{g}/\text{m}^3$  (30). The sampling sites were in an air basin shared by residential areas and fields treated with MS by center-pivot overhead sprinkler irrigation. On the basis of typical environmental conditions in Washington state during MS application (29), this maximum would have occurred at about 1.5 km downwind, near or within residential areas. The results of these various studies indicate that drip irrigation will give the least air concentrations and by implication will have the lowest emission rates for MITC. For example, in a study similar to ours where MS was applied by surface drip irrigation in the centers of planting rows, just below a plastic tarp, air concentrations ranged up to 35  $\mu\text{g}/\text{m}^3$  for downwind distances of 12–21 m (31). However, surface chemigation is more cost-effective, since this application method does not require special field preparation, as does drip irrigation. A recent study showed that additional intermittent postapplication waterings could reduce emissions for surface chemigation, and for the alternative shank injection, by an order-of-magnitude (32). But, emission rates would still be an order-of-magnitude greater than emissions for drip irrigation, as employed in the present study.

The acute ( $\sim 24$  h) inhalation reference exposure level (REL) for MITC is 66  $\mu\text{g}/\text{m}^3$  (33). REL is the concentration level at or below which no adverse health effects are anticipated for a

specified exposure duration (33). The subchronic REL ( $\geq 15$  days) is estimated to be about  $3 \mu\text{g}/\text{m}^3$  (33). These RELs are based on inhalation and eye irritation studies with rats and human volunteers (34, 35). For all of the sampling stations in our study, integrated, 48 h average concentrations for MITC in air resulting from subsurface drip irrigation were below the REL,  $24 \mu\text{g}/\text{m}^3$  for field 1 and  $14 \mu\text{g}/\text{m}^3$  for field 2. At no time did field personnel detect any appreciable odor as they worked close to the treated fields, even during application. Typical exposure for the field personnel during each sampling period was about an hour, the time necessary to service all of the field sampling stations.

**Field Modeling.** The evaporative flux values for the application period derived from the ISCST3 model were essentially the same as the value derived from correlation techniques: the average for the two fields was about  $4.06 \mu\text{g}/(\text{m}^2 \cdot \text{s})$  (ISCST3) compared to  $4.28 \mu\text{g}/(\text{m}^2 \cdot \text{s})$  (correlation). In an independent study, a flux value of  $4.30 \mu\text{g}/(\text{m}^2 \cdot \text{s})$  was determined for MITC from a surface drip irrigation under a plastic tarp (31). These investigators also observed an MITC loss over the first 48 h of about 2.32% of the applied material due to volatilization. By comparison, plotting the data in **Table 3** for field 2 versus sampling period and then integrating the area under the resulting curve led to an estimated loss of about 1.4% of the applied material due to volatilization over the 48 h sampling period. While the two loss values are the same order-of-magnitude, we would expect to observe a lower value due to drip irrigation at depth (10 cm) compared to surface drip irrigation. This comparison suggests that the estimated evaporative flux value of  $4.3 \mu\text{g}/(\text{m}^2 \cdot \text{s})$ , averaged over the first 12 h, would have been somewhat greater during the first four hours, as indicated by the loss rate (31).

The estimated emission rates for MITC, resulting from subsurface drip irrigation, were about 1–2 orders-of-magnitude less than emission rates for MITC from other common methods of application. Other investigators have found that for surface chemigation and shank injection, using standard water seal, measured emission rates were in the range 300–400  $\mu\text{g}/(\text{m}^2 \cdot \text{s})$  (32). However, by using an 'intermittent water seal', where the same amount of water was applied ( $\sim 3.8$  cm) but divided up into a greater number of smaller applications, emission rates were reduced to 23  $\mu\text{g}/(\text{m}^2 \cdot \text{s})$  (shank injection) and 93  $\mu\text{g}/(\text{m}^2 \cdot \text{s})$  (surface chemigation). These emission rates are similar to 80  $\mu\text{g}/(\text{m}^2 \cdot \text{s})$  estimated, using an atmospheric dispersion model with meteorological data measured at the field (36), for a center-pivot field treated by an overhead sprinkler system under relatively cool environmental conditions (29). Although intermittent water seal and/or cool weather conditions may attenuate MITC emission rates, emissions from subsurface drip irrigation would still be about an order-of-magnitude less.

Emission rate, coupled with atmospheric dispersion models (19, 37), can be used as a basis for estimating and assessing downwind exposure to MITC. For example, using  $4.06 \mu\text{g}/(\text{m}^2 \cdot \text{s})$ , along with the meteorological conditions, as input to a Gaussian plume dispersion model (37), estimated concentrations for MITC 1.6 km downwind, at a public park, were about 4–7  $\mu\text{g}/\text{m}^3$ ; at 3.2 km downwind, at a township, the estimated concentrations were  $< 2 \mu\text{g}/\text{m}^3$ . These estimated concentrations are an order-of-magnitude less than the acute REL for MITC (i.e.,  $66 \mu\text{g}/\text{m}^3$ ) (33), and these are the worst-case values during MS application, which in our study lasted at the most about 4 h. During postapplication periods, these

concentrations would decrease as MITC emission rate declined over time. Other methods of application, such as surface chemigation and shank injection, would be expected to result in MITC concentrations, at the same downwind distances, 1–3 orders-of-magnitude greater, depending on the weather and method of water seal used. Recent monitoring studies in Washington state showed that for surface chemigation—center pivot, overhead sprinkler—many of the MITC samples had concentrations in air near residential areas that exceeded both the acute ( $66 \mu\text{g}/\text{m}^3$  ( $\sim 1$  day)) and subchronic ( $3 \mu\text{g}/\text{m}^3$  ( $\geq 15$  days)) REL values for inhalation exposure (33).

Our sampling and analysis methods described here proved to be useful for the reliable determination of MITC in air near fields treated with MS by subsurface drip irrigation. This application method gave measured residues in air up to four orders-of-magnitude less than residue levels typically observed for surface chemigation application methods. Furthermore, MITC emission rates estimated for our study fields were up to two orders-of-magnitude less than emission rates estimated for surface chemigation methods. Because of the lower emission rates, our measured and estimated concentrations of MITC in downwind air resulting from subsurface drip irrigation were not at levels of regulatory health concern.

## SAFETY

MITC is a strong ocular and respiratory tract irritant. There is no clear-cut evidence for carcinogenicity.

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