Estimating Methyl Isothiocyanate Emission Rates Following Soil Incorporated Shank And Modified Center Pivot Chemigation Metam Sodium Applications

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Summary: An air sampling program was conducted in Franklin County, WA in the fall of 2008 to monitor fumigant air movement at near-field receptor locations following low drift (drizzle boom) modified center pivot chemigation and soil-incorporated shank injection applications with Sectagon 42® (42% metam sodium). This study was developed to assess emission rates and total cumulative field loss of metam sodium's gaseous by-product, methyl isothiocyanate (MITC) during and four days post-application under conditions typical for Pacific Northwest potato pre-plant fumigation. The aim of this work is to aid growers in evaluating putative reduced emission application practices particularly when deciding on application practices/timing near residential communities. We also developed this study to provide regionally specific MITC emission rate information to the United States Environmental Protection Agency Office of Pesticide Programs. As a result, this field demonstration closely adhered to Series 875 of the U.S. EPA Pesticide Assessment Guidelines: Occupational and Residential Exposure Test Guidelines. For each treatment plot, MITC concentrations (in $\mu g\ m^{-3}$) were generated from air collected through activated charcoal at eight receptors spaced around each test plot periphery before, during, and throughout the 4-day post application period. For each treatment plot, MITC field emission rates ($\mu g\ m^{-2}\ sec^{-1}$) together with total cumulative MITC loss were estimated using an Industrial Source Complex Short Term (ISCST3) emissions model that utilized hourly meteorological data gathered at the field study location over the study time frame. Estimated total cumulative MITC loss by drizzle boom was 47% and 12.6% by soil incorporated shank injection. Procedures for emission rate estimation acceptance followed California Department of Pesticide Regulations criteria for soundness of fit of field-measured to model-predicted near-field emission estimates.

Introduction

Starting in 2005, metam sodium along with other methyldithiocarbamate salts underwent a re-registration review overseen by EPA Office of Pesticide Programs (EPA-OPP or Agency) leading to a July 2008 re-registration eligibility decision (RED;US EPA 2008). Several field-scale monitoring studies that estimated volatilization flux density (flux) emissions of MITC were employed for buffer zone mitigation setting. Flux studies specific to the Pacific Northwest cooler fall season application conditions were not available as part of the RED assessment. Because of the absence of PNW regional flux information, the Agency relied on emission data from smaller acreage row crop summer application studies in southern California to calculate field edge buffer zones for larger acreage field crop fumigations in the PNW. These field emission data sets are limited in their utility because they provide results only for the specific conditions under which the study was conducted. Based on regional field acreage, application rates, and chemigation practices specific to the PNW, the current RED tabulated emission data can result in appreciable field-edge buffers. Since large segments of potato growing acreage exist in close proximity to residential communities, strict adherence to the current RED buffer zone criteria could have serious economic implications throughout the PNW. The Agency has given a limited window for PNW fumigant emission flux data to be generated; however, label language changes may be forthcoming as soon as 2010 (US EPA 2008).

Methods

To help fill this needed fumigant emissions data gap, Sectagon 42 was applied to two treatment plots (1.7 acres for drizzle boom and 1.8 acres for shank injection) within a 122 acre field circle located in Franklin Co. WA to assess near-field MITC air emissions before, during, and through 4-days post application (from October 8th through the 13th). The chemigation and shank field plot locations were meteorologically positioned within this field to best minimize MITC cross-interference (Figure 1).

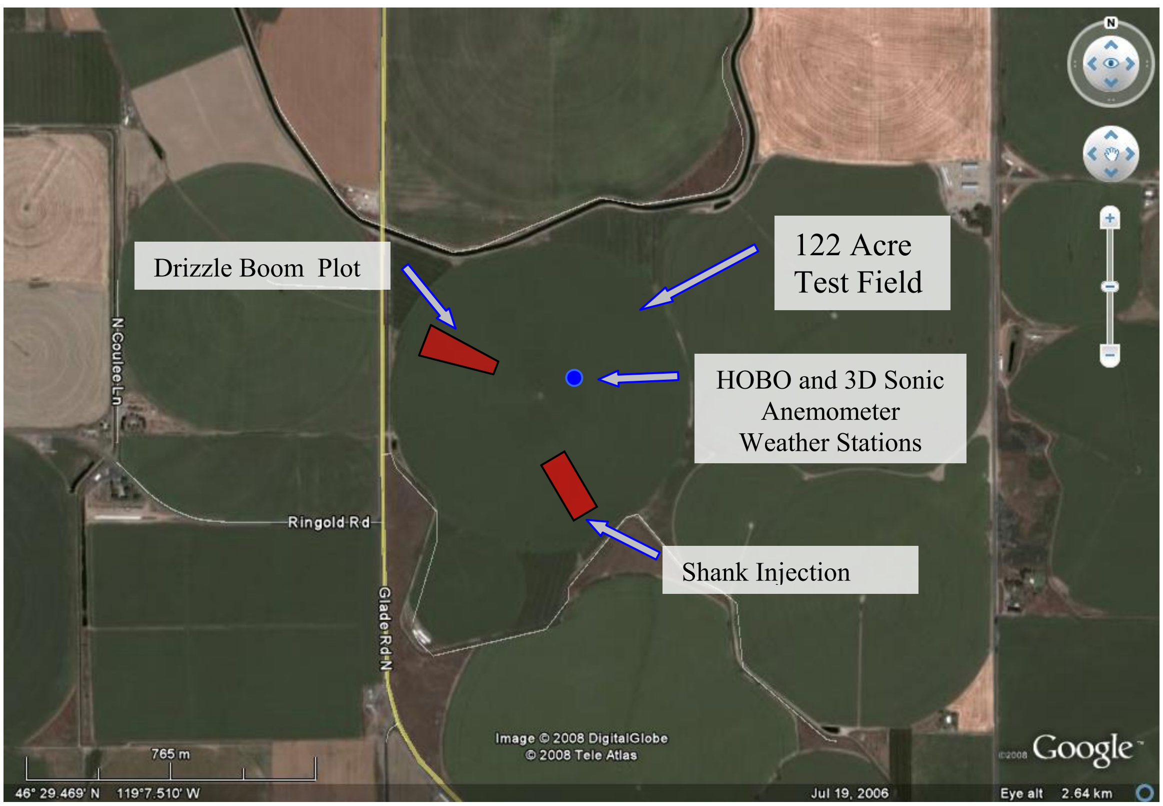

Figure 1: Field Demonstration Test Site. Franklin County, Washington State

A HOBO weather station was positioned near the center of the circle pivot to collect air/soil temperature, and soil moisture data over the study time frame and the CSAT3 3-D sonic anemometer employed to collect wind speed/direction data. The plots were positioned at these northwesterly and southeasterly locations to minimize MITC cross contamination from anticipated southwesterly prevailing winds over the study time frame.

Both fumigation applications were conducted concurrently on October 8th. To have both applications end at approximately the same time, the drizzle boom chemigation was started ca. 1-

hour earlier. For each treatment plot, MITC in air was continuously monitored by activated charcoal cartridges at eight sampling site receptor locations closely surrounding the plot periphery before, during, and throughout the 4-day post application period. The air sampling pumps were operated at ca. four-hour sampling intervals before, during, and through two-days post application. Eight-hour interval sampling was conducted on post-application days three and four. For each treatment plot, MITC concentrations (in µg m^{-3}) were generated from air collected through activated charcoal at eight receptors spaced around each test plot periphery before, during, and throughout the 4-day post application period. For each treatment plot, MITC field emission rates (µg m^{-2} sec^{-1}) together with total cumulative loss of MITC via the air pathway were estimated using an Industrial Source Complex Short Term (ISCST3) emissions model that utilized hourly meteorological data gathered at the field study location over the emission study time frame. The generated emission rate estimates and total cumulative losses for each treatment plot reported herein were performed by Sullivan Environmental Consulting using the CSAT data set together with measured airborne MITC concentration data supplied by the WSU-Food and Environmental Quality Laboratory. A more detailed regulatory analytical summary report (Littke et al., 2009) describing field procedures, analytical methods/quality control, and emission estimation procedures has been provided to the WSPC.

Results

Field-Measured MITC Concentrations: MITC air concentrations (i.e., the averaged MITC concentration from the eight air sampling receptors per interval sampling date) over the 4-day study time frame are summarized in Table 1. Here we observed that averaged whole field concentrations peaked during the 4-hours post application for drizzle boom modified center-pivot chemigation (417 µg m^{-3} (138 ppb)) with a maximum single observation near-field concentration during this time of 963 µg m^{-3} (318 ppb). Maximum whole field-averaged MITC concentrations of 78 µg m^{-3} (26 ppb) were observed 16-hours post application for the shank treated field with a maximum single observation near-field concentration of 122 µg m^{-3} (40 ppb) registered during this same 16-20 hour receptor period. Table 2 lists the maximum single cartridge air concentrations detected during the course of the chemigation and shank injection fumigation events.

From current regulatory inhalation exposure criteria, drizzle boom maximum downwind MITC concentrations exceeded by 4-fold the EPA OPP acute level of concern (LOC) value of 22 ppb, and were higher than the EPA no observable adverse effect level (NOAEL) of 220 ppb both during application and for the first 4 hours post application. Measured maximum downwind MITC air concentrations were lower than 22 ppb for all monitored periods for shank injection except for a 4 hour period starting 16 hours post application. Between 16 and 20 hours post-shank, the maximum observed single air monitor concentration of 40 ppb (122 µg m^{-3}) was observed. Measured MITC concentrations from air monitoring receptor locations positioned equidistantly between the two test plots indicate downwind emissions towards the shank plot over this interval period. Although receptors were positioned at test plots to minimize cross-contamination, it is reasonable to state that directional MITC drizzle boom source emissions contributed to the lower measured shank emission estimates, especially during the first 20 hours of this field demonstration.

Table 1
Whole Field Averaged MITC Concentrations

Approximate Hours post fumigation	Assigned Period	Drizzle Boom average[1] MITC air concentration ($\mu g/m^3$)	(ppb)[2]	Shank Injection average[1] MITC air concentration ($\mu g/m^3$)	(ppb)[2]
Pre application		0.67	0.22	0.54	0.18
Application	1	280	92.4	9.64	3.18
4	2	417	138	17.0	5.61
8	3	226	74.6	14.5	4.79
12	4	122	40.3	17.4	5.74
16	5	179	59.1	77.9	26.0
20	6	47.1	15.5	38.1	12.6
24	7	26.5	8.75	12.2	4.03
28	8	47.5	15.7	3.92	1.29
32	9	43.6	14.4	5.97	1.97
36	10	17.3	5.71	4.22	1.39
40	11	31.7	10.5	3.22	1.06
44	12	12.3	4.06	3.90	1.29
48	13	7.76	2.56	4.17	1.38
52	14	10.9	3.60	2.14	0.71
56	15	15.6	5.15	10.6	3.50
64	16	30.1	9.93	9.52	3.14
72	17	10.3	3.40	2.53	0.84
80	18	25.2	8.32	9.56	3.15
88	19	19.5	6.44	6.45	2.13
96	20	14.9	4.92	5.47	1.81

[1] Average value represent an average concentration of the eight samples, i.e. DB1-DB8, SH1-SH8

[2] $\text{MITC ppb} = (\mu g\ m^{-3}) \times \frac{(8.21 \times 10^{-2}\ \text{L-atm/mole-}^{o}\text{K})\ (298^{o}\text{K})}{(73.12\ \text{gram/mole})\ (1\ \text{atm})}$

Table 2
Maximum Measured MITC air concentrations

Receptor identification	Maximum receptor air concentration detected ($\mu g/m^3$)
Drizzle Boom Field Plot air sample DB7-R, 4-hr post application	963 (318 ppb)
Shank Injection Field Plot air sample SH5 16-hr post application	122 (40 ppb)

MITC Emission Rate Assessment: To assess the potential for bystander exposure in a manner consistent with practices employed by state and federal regulatory agencies, MITC volatilization density (flux) in units mass/surface area/time together with total cumulative loss were estimated using a steady-state Gaussian plume algorithm and California Department of Pesticide Regulations (Cal DPR) back calculation approach from the collected receptor emission and gathered meteorological data according to procedures from Ross et al. (1999) and Johnson et al. (1999). This least-squares technique regressed field-measured to model-predicted emissions over the 4-day experimental timeframe. Stability classes were determined according to Pasquill-Gifford stability methodology, using wind speed and cloud cover for each hour interval over the study time frame. California Department of Pesticide Regulations (Cal DPR, 2006) Emissions Assessment Method criteria was used to assess the best means for estimating MITC flux during each interval period for the drizzle boom and shank application test plots. Emission estimations were considered reliable if linear regression of the measured and normalized modeled data were well correlated (i.e, slope of regression line had a significance > 95th percent confidence level) and the intercept term was not significant (signifying the 95th percent confidence level included the origin). If the least squares slope was not significant, then the mean measured concentrations divided by the mean modeled concentrations was conservatively employed to calculate the emission rate for that period. Following this regulatory technical procedure for estimate fit, the estimated total cumulative MITC loss by drizzle boom was calculated to be 47% compared to 12.6% by soil incorporated shank injection. Figure 2 illustrates the relative emission rates of drizzle boom to shank over the continuous 4-day application/post application time frame.

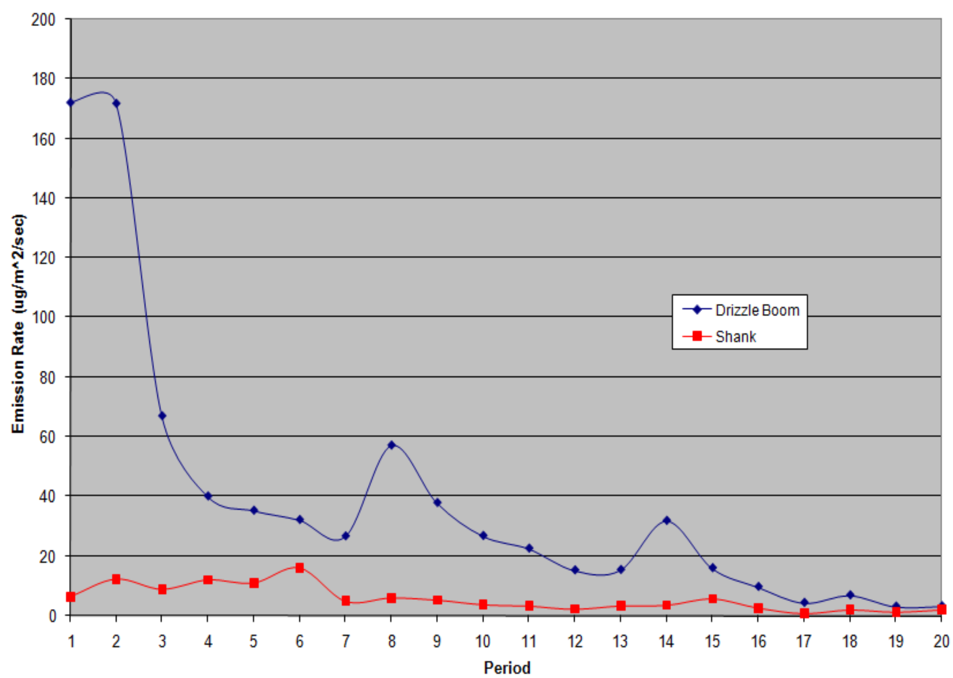

Figure 2: Comparison of Drizzle Boom and Shank Injection Emission Rates: October 8th through the 13th 2008, Franklin County, WA
(see Table 1 for interval sampling hours corresponding to each period)

Estimated low drizzle boom background MITC contributions during the early periods of this study resulted in use of the more conservative mean measured/mean flux estimation approach for the shanks test plot at application and up to the first five post-application periods. The occurrence of low MITC emissions at two off-field receptor locations approximately equidistant between the two test plots further corroborated that concentrations from the drizzle boom test plot contributed to MITC concentrations at the more northwesterly shank receptor locations. When defaulting to a more conservative approach, it is reasonable to anticipate over-estimation of actual field measured MITC emission rates. This especially would be expected at the shank plot where higher near-field source contributions can mask actual low field receptor emissions.

Acknowledgements

This proceedings represents the culmination of a proactive and collaborative research/outreach effort for providing much needed regionally specific MITC emission rate data typical of the cooler fall climatic conditions when PNW fumigations are occurring. This effort involved university research/extension specialists, experts in the area of field volatilization flux density measurements, potato growers, commodity group representatives, and pest management field advisors. Special thanks must go to many for providing their *in-kind* support leading the completion of this report. Particularly, I wish to thank Ed Schneider of Schneider Farms for donating use of his land-chemigation equipment, Monte Spence of WindFlow Fertilizer for retrofitting, center pivot drizzle boom operations/application oversight, Jim Ossman of Crop Production Services for their *in-kind* efforts in performing the concurrent shank application, Kurt Volker-Jim Owens from Tessenderlo Kerley for *in-kind* product support, and David Sullivan and his group from of Sullivan Environmental Consulting for rigorously assuring the quality of the emission rate estimations reported herein. The Food and Environmental Laboratory faculty/staff are appreciative to all who actively participated in the up-front planning, concurrent fumigant applications, field emission monitoring, and data verification that has lead to the information provided in this proceedings.

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