

EFFECT OF SOIL APPLICATION METHOD ON SURFACE EMISSION RATES OF  
METHYL ISOTHIOCYANATE

By

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To the Faculty of Washington State University:

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I would like to dedicate this work to my wife Becky, and my daughters Graceanna, Karissa and Tegan. Without your encouragement and help this work would not have been possible.

EFFECT OF SOIL APPLICATION METHOD ON SURFACE EMISSION RATES OF  
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Abstract

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An agronomic field-scale air monitoring study was conducted in eastern Washington State in the fall of 2008 to estimate surface volatilization of methyl isothiocyanate (MITC) following concurrent low drift center pivot chemigation (drizzle boom) and soil-incorporated shank injection applications of metam sodium. The aim of this project was to side-by-side compare MITC off-gassing under application rates and climatic conditions typical for cooler fall Pacific Northwest pre-plant potato fumigation. A second aim of this work was to provide relevant MITC emission rate data for these putative emission-reducing application practices to aid in human health risk assessments in setting conservatively protective field-edge set-back distances from treated fields. The results indicated that MITC near-field emissions are appreciably reduced by shank injection compared to center pivot fumigation even with adoption of irrigation system modifications that reduce physical drift. This study suggests that surface volatilization will continue to be a major factor in MITC off-target movement and that adoption of shank injection near areas of residential development should be encouraged to mitigate emissions as much as possible.

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## Acronyms and Abbreviations

American Meteorological Society/Environmental Protection Agency Regulatory Model	AERMOD
California Department of Pesticide Regulations	CALDPR
California Puff Model	CALPUFF
Clean Air Act Amendments	CAAA
Environmental Protection Agency	EPA
Hazardous Air Pollutant	HAP
Industrial Source Complex Short Term	ISC-ST
Lethal Dose for 50% of Population	LD <sub>50</sub>
Level of Concern	LOC
Lowest Observed Effects Level	LOEL
Margin of Exposure	MOE
Metam Sodium	Metam
Methyl isocyanate	MIC
Methyl isothiocyanate	MITC
No Observed Effects Level	NOEL
Pasquill Stability Class	PSC
Probabilistic Exposure and Risk Model for FUMigants	PERFUM
Reference Exposure Level	REL
Reregistration Eligibility Decision	RED
Volumetric Water Content	VWC

## Preface

In this work Chapter 1, “Literature Review” covering both the “History and Usage of Metam Sodium” as well as the “Measuring/Calculating Flux of MITC” addresses the relevant literature as to why the need for reducing the offsite movement of MITC through changes in agricultural practices is necessary. Understanding the factors that influence fumigant emission rates from one medium to another, in this case soil/water to air gives insight into potential changes in agricultural practices that may reduce the potential for offsite movement. Many different methods can be used to measure flux of compounds, understanding which one is the most relevant for MITC is critical.

Chapter 2, “Estimating Methyl Isothiocyanate Emission Rates following Soil Incorporated Shank Injection and Modified Center Pivot Fumigation” is a manuscript prepared for submission to Atmospheric Environment, and was authored by Mr. Littke in place of a traditional master’s thesis. This work was also presented at the American Chemical Society National Meeting in Washington DC in 2009. Chapter 3 discusses conclusions from this study and possible future considerations in reducing offsite movement of airborne fumigants such as MITC.

Attachment A is the Analytic Summary Report as posted on the FEQL website detailing this 2008 near field airborne MITC concentrations and flux work encompassing both drizzle boom modified center pivot chemigation and shank injection. Attachment A was submitted to the EPA to provide relevant flux information for the Pacific Northwest Region in response to potential changes listed in the Reregistration Eligibility Decision for metam sodium.

## CHAPTER 1. LITERATURE REVIEW

### A. HISTORY AND USAGE OF METAM SODIUM

#### History of Metam sodium

Metam sodium (sodium methylthiocarbamate) is a widely used soil fumigant in row and field crop production in the United States. First marketed in the 1950's, metam sodium has been sold under the trade names Amvac Metam Sodium®, Busan®, Metam CLR™ 42%, Sectagon 42®, and Vapam®. Metam-sodium (metam) is seen as one of replacements for methyl bromide, which was phased out by the EPA under the Clean Air Act in 2001 after being characterized as a Class I Stratospheric Ozone Depleting Substance.

Metam was first registered with the EPA in 1975, primarily for control of soil borne nematodes, soil fungi, insects, and weed seeds (US EPA 2009). This substance is a valuable pre-plant soil fumigant for Pacific Northwest growers in combating soil borne pests and pathogens in large production crop systems. Its usage is generally credited with an increase in crop production worth almost \$250 per acre (\$48 million/year) in Washington and \$800 per acre (\$8 million/year) in California (Chandgoyal and Berwald 2007). However methyl isothiocyanate (MITC), the gaseous bioactive product responsible for pest control, has the potential to move off-target thereby adversely impacting nearby residential populations.

Finding a balance between grower reliance on metam sodium and protecting nearby residential communities from inhalation exposure from MITC movement will be a challenge; especially as communities expand into historically traditional agricultural regions. Understanding environmental factors and how improvements in application technology can aid in minimizing MITC will be critical. This review provides an overview of the influence of

environmental factors on surface volatilization and laboratory assessment methods used to estimate MITC emission rates (i.e., flux). It is the hope that this review and applied field research will provide information to both the grower community and regulators when deciding which type of application technique to use/allow near residential communities.

### Chemical Characteristics of Metam-sodium and MITC

Metam-sodium (sodium methylthiocarbamate; metam) is a member of a class of pesticides known as dithiocarbamates. Metam has the molecular formula  $C_2H_4NNaS_2$  with a molecular weight of 129.18. Chemical characteristics for this substance are presented in Table 1.1.

Concentrated metam-sodium is a stable compound in aqueous solution, but degrades quickly in the presence of acids and salts of heavy minerals (Draper and Wakeham 1993, Ruzo, 2006). At neutral and basic pH metam quickly transforms into MITC and hydrogen sulfide. Under acidic conditions, carbon disulfide, hydrogen sulfide, methylamine and MITC are principle transformation products (Draper and Wakeham 1993, Geddes et al 1995).

On contact with soil, metam-sodium rapidly converts to methyl isothiocyanate (MITC; Smelt and Leistra 1974). Depending on soil temperature and moisture, over 90% of applied metam-sodium can be converted to gaseous MITC in two hours or less (Gerstl et al 1977). The vapor pressure for this highly volatile degradate has been estimated to be ca. 20 mmHg at 20 °C (Rubin 2002). The chemical characteristics for MITC can be found in Table 1.2. Although MITC can rapidly diffuse and be retained in properly wetted soil, a portion will eventually be lost by volatilization to the atmosphere (Dungan et al 2003, Zheng et al 2006, Candole et al 2007).

Atmospheric transformation products from MITC may warrant a human health concern. Direct photolysis of MITC in part transforms to methyl isocyanate (MIC) (Geddes et al. 1995). Methyl isocyanate is more toxic than MITC and is listed as a hazardous air pollutant (HAP) under the Federal Clean Air Act Amendments of 1990 (CAAA-90). This Act requires extensive testing of HAPs including their transformations and fate in the atmosphere downwind from release. Moreover, MIC may be photochemically stable and as such have toxicologically relevant human exposure residence times in the troposphere. Geddes et al (1995) also identified methyl isocyanide ( $\text{CH}_3\text{NC}$ ), methylamine ( $\text{CH}_3\text{NH}_2$ ), N-methylformamide ( $\text{CH}_3\text{NHC}(\text{O})\text{H}$ ), sulfur dioxide ( $\text{SO}_2$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ) and carbonyl sulfide ( $\text{C}(\text{O})\text{S}$ ) as other likely gas-phase photochemical transformation products from MITC. Aqueous metam-sodium transforms in sunlight into several compounds including MITC, methylthiourea, and 1,3-dimethylthiourea (Draper and Wakeham 1993).

### Toxicology Associated with Metam and MITC

Metam-sodium: Acute dermal  $\text{LD}_{50}$  of metam sodium in mice, is  $750\text{mg kg}^{-1}$  (Pruett et al 2001). The acute oral  $\text{LD}_{50}$  in birds is  $211\text{mg kg}^{-1}$  (USEPA 2009). The NOAEL (no observable adverse effects level) for dermal exposure was  $31.25\text{ mg kg}^{-1}\text{ day}^{-1}$ . Higher doses caused arrhythmia, edema and dermatitis in several test subjects (Rubin 2003). The major route for toxicity of metam-sodium is believed to occur via dermal exposure during applicator mixing-loading and other occupational situations (Rubin 2003).

The acute oral NOAEL was set at  $5\text{mg kg}^{-1}\text{ day}^{-1}$  based on two separate studies with rats and later with rabbits. Skeletal deformities and developmental effects, including suppression of body weights and decreased food consumption occurred at higher concentrations. Sub chronic

oral NOAEL levels were established at  $0.3 \text{ mg kg}^{-1} \text{ day}^{-1}$  based upon a 90-day dietary exposure study with dogs. Higher doses in the subchronic study caused liver pathologies (Rubin 2003).

MITC: Exposure to MITC is thought to occur primarily via inhalation or dermal routes. Acute oral toxicity studies with rats generated a  $\text{LD}_{50}$  of  $55 \text{ mg kg}^{-1}$  in females and  $82 \text{ mg kg}^{-1}$  in males (Rubin 2002). Inhalation studies with rats showed a 1-hour  $\text{LC}_{50}$  of 633 part per million (ppm) and a 4-hour  $\text{LC}_{50}$  of 180 ppm. A 4-week inhalation toxicity study in rats, established a lowest observable adverse effect level (LOAEL) of 1.7 ppm. After exposure to 34 ppm MITC for 6 hours a day, 5 days a week rats had developed bronchopneumonia, emphysema, bronchial and tracheal epithelial proliferation, rhinitis, focal metaplasia, and had increases in lung weight and decreases in body weight. The estimated LOAEL for human exposure of 300 ppb was estimated using the rodent LOAEL generated using Haber's Law to convert from 6 hours  $\text{day}^{-1}$  (in the study) into 24 hours  $\text{day}^{-1}$  (expected human exposure). An estimated critical subchronic NOAEL of 100 ppb was generated by applying a default factor of 3 to the rodent LOAEL to account for uncertainty in intra-population susceptibility (Rubin 2002). Human subjects exposed to MITC and assessed irritation response (e.g. tearing, blinking). No response was observed at 220 ppb (the NOAEL), but responses were at 800 ppb (the LOAEL) (Rubin 2002).

MITC is an acute respiratory irritant (Pruett et al 2001). Residential exposure incidences have documented nose irritation, sore throat, nausea, and dizziness (Thongsinthusak 2003). Public health regulatory Reference Exposure Levels (REL's) also known as Level of Concern (LOC) for MITC are based upon NOAEL generated with the eye exposure data and adjusted for additional intra-population uncertainty (10 fold decrease). The REL as listed by the EPA, for 8 hour inhalation MITC exposure is 22 ppb (NOEL of 220 ppb/ 10). The subchronic REL of 1 ppb

is based upon the LOAEL of 100 ppb, with a 10 fold factor for intra-human variability and another 10 fold factor due to extrapolation of the LOAEL from an animal study (Rubin 2002).

Exposure studies have not been conducted using the full range of compounds in the degradation pathway of metam. The potential exists for either additive or synergistic effects (Rubin 2002). The degradation products MIC and hydrogen sulfide have been shown to have negative impacts on human health. Currently the EPA is asking for more studies, to better understand the impact of exposure and to protect human health (EPA 2009).

### Incident Exposures Associated with Metam and MITC

Several major spills of metam-sodium have caused environmental harm and raised health concerns for local residential areas. In 1991, a railcar full of metam crashed into the Sacramento River near Dunsmuir, CA. As a result both residents and clean-up crews were exposed to high levels of MITC. Monitored air concentrations of 0.2-37ppb were observed three days post incident. Over 700 people sought medical attention for headaches, nausea, eye irritation, dizziness, shortness of breathe and diarrhea (Pruett and Myers 2001). In addition twenty people were diagnosed with reactive airway disorder (RAD), a type of chemically induced asthma (Cone et al 1994, O'Malley 2004). During 1999 Earlimart, CA was the scene of another major incident in which 171 complaints related to exposure were filed. Gaseous MITC emissions from an agricultural application on the north side of town caused complaints that ranged from nausea and eye irritation to respiratory illness and asthma. Estimated MITC concentrations in air using computer modeling ranged from 0.5ppm to as high as 1ppm; ca. 50-fold higher than the 22 ppb EPA level of concern (LOC) (O'Malley 2004).

Metam-sodium is widely used in the Pacific Northwest to treat agricultural fields in large-scale potato production. Recent 2008 residential air monitoring programs conducted in Washington State (Merriman and Hebert 2007, WSU FEQL 2008 and 2009) also indicate that MITC air concentrations can appreciably exceed both EPA acute and chronic LOC during fall season pre-plant agricultural fumigation practices. Sampling was timed to coincide with the majority of fumigations for this area. Air monitoring at residential locations in west Pasco, Washington State measured MITC air concentrations that exceeded 10-fold (ca. 220 ppb) the acute EPA LOC of 22 ppb on a single day. The EPA short-term exposure level (5ppb over a 24-hour period) was exceeded in 3 days in 2007 and 5 days in 2008 (WSU FEQL 2008 and 2009). This Washington State air monitoring program consistently indicates that MITC air concentrations can exceed federal acute and short-term regulatory human health inhalation exposure criteria in this important agricultural region now facing expansive urban and commercial development.

## B. MEASURING/CALCULATING FLUX OF MITC

### Measuring Emissions

Flux is a volatilization rate expression that describes the chemical mass volatilizing from the ground and entering the atmosphere per unit area per unit time. Several methods for generating flux measurements for soil applied fumigants exist including, direct in-field aerodynamic measurement, energy balance, integrated horizontal flux (IHF), theoretical profile

shape method (TPS), eddy correlation, and near-field back calculations using computer air dispersion modeling.

Direct flux measurements are made by using a chamber over the soil surface to directly collect pesticide residues in air. Air is drawn through the chamber into a sampling tube usually fitted with a charcoal filter trap. The sample is then analyzed and corrected to reflect the original surface area as well as the flow rate, and air volume inside the chamber.

Direct flux measurements allow testing of only a portion of the air in the chamber (Papiernik et al. 2004a). This method has benefit when used in the laboratory to test several different factors possibly influencing fumigant emissions. Researchers can control environmental factors, and change several variables to see the influence on flux, including depth of injection, rate of application, soil moisture content, temperature and organic content of soil that would simply be impractical on a large field scale. Drawbacks to the technique include requiring several chambers over a large area to get an average flux value for field research, which limits its utility to the small fields or laboratory research (Ou et al 2006). Because temperatures inside the chambers could be higher than ambient temperature, actual flux values may be lower than those measured.

Energy balance method uses soil heat flux to determine the flux of compounds. It calculates flux by assuming the flux of water is equal to flux of the compound of interest. Pesticide flux is calculated by using the Bowen ratio, i.e. the ratio of sensible (energy needed to heat soil without causing evaporation) to latent heat flux (heat from the soil to the atmosphere, usually associated with evaporation), which is proportional to the ratio of air temperature and water vapor pressure. For this method solar radiation detectors are required as well as

temperature recordings. This method is not suited for periods when the sensible heat flux is equal to the latent heat flux which can occur in evening periods (Majewski et al 1990).

Eddy correlation (EC) method uses sensors to measure the amount of a compound in an air stream over time. By knowing the concentration and the speed and direction of the wind current the flux of the compound can be determined. The use of this method is determined by the availability of sensors to detect real time concentrations of the compound of interest. Also a 3-D sonic anemometer is required to precisely measure both the vertical and horizontal movement of air currents. This method is accurate in both low and high wind situations, however the cost and availability of the equipment limits its use (Majewski et al 1990).

Integrated horizontal flux (IHF) and theoretical shape profile (TSP) methods are based upon a two dimensional trajectory simulation model that has been shown to be in good agreement with observed vertical profiles of horizontal flux at the center of a circle (Wilson et al 1983, Majewski et al 1990). Both IHF and TSP require a circular plot with the sampling device in the center of the plot, negating any changes in wind direction since it will always be blowing toward the center across the same distance of treated ground. The IHF methods rely on air samplers and wind speed/direction at several heights at a single location, but TSP methods use only one sampler and wind speed/direction monitor (Ferrari et al 2003). TSP is reliant upon correctly determining the surface roughness length, or height at which horizontal and vertical flux are equal. The advantage of TSP over IHF is that only a single sampling device is needed. Reliance upon a single sampler for information could be undesirable, if problems arise. The ability to perform experiments on smaller plots, due to the lack of a long fetch, needed for other methods also makes TSP and IHF attractive. At low or no wind speeds determination of flux

may be a problem (Majewski et al 1990). The increased cost of multiple air samplers and wind speed/direction monitors at multiple heights can make IHF cost prohibitive.

The aerodynamic method is similar to both the IHF and TSP methods, but allows for air samplers to be located off site and also allows for irregular field shapes instead of only circular plots. The theory is that the flux density is consistent from the ground to at least 2m up to 20m with stable conditions, provided the fetch is large enough. The distance from the leading edge of the application to the samplers (commonly known as fetch), should be approximately 100 times the height of the samplers (van Wesenbeeck et al 2007). Estimations of flux at the measured height should be similar to flux at the ground level. Aerodynamic method has been used by several agencies including California Department of Pesticide Regulation (Cal DPR) to estimate flux of MITC under different conditions using Gaussian plume air dispersion models (CEPA 1994, Wofford et al 1994, CEPA 1997).

Bosanquet and Pearson are considered the early pioneers of Gaussian plume air dispersion modeling. Their equations developed in the 1930's led to modern complex computer models. Sutton (1947a, 1947b), help develop the Gaussian equations used in the current air dispersion models in response to the need to understand the movement of chemical weapons after detonation, as well as the more reasonable understanding of dispersion of pollutants from industrial stacks. Computer dispersion models have been used by CAL DPR and the EPA Office of Pesticide Programs (EPA-OPP) to estimate flux of many soil fumigants including metam-sodium. Atmospheric dispersion models are both a mathematical simulation of the physics and chemistry governing the transport, dispersion and transformation of pollutants in the atmosphere; and means of estimating downwind air pollution concentrations given information about the pollutant emissions and atmospheric characteristics. Air dispersion models allow users to

estimate flux/emissions by “back calculating” comparing known air concentrations to concentrations generated using the model.

The Gaussian equation, which is the basis for the Industrial Source Complex Short Term (ISCST3) and California Puff (CALPUFF) models used in estimating fumigant emission rates, relies on a proportional relationship between flux and concentration where increases in flux are directly correlated to an increase in concentration. This proportional relationship allows the back calculation of flux from measured air concentrations collected at near field receptors. Both Gaussian models allow the user to create a GPS coordinate representation of the field that includes near-field air monitoring receptor locations for modeling flux., Weather data, either from onsite (preferred) or nearby is essential for the estimation of flux to be accurate. Both models use the surface area of the field as the source of the material being studied. A default estimate of flux rate is required for comparing actual to modeled predictions. This estimate does not need to be accurate, but the computer model generates air concentrations at the receptors (actual air monitoring stations) based upon the estimate. These modeled concentrations are then compared to the actual measured concentrations. Generally the initial model is run at a default flux value of  $100\mu\text{g m}^{-2}\text{sec}^{-1}$  (Johnson et al 1999). The model is run under the actual weather conditions during the time period, to produce modeled air concentrations at the location of the actual air samplers in relation to the field.

The initial modeled air concentrations are then compared to the actual measured concentrations by using linear regression. The regression slope should be significant at the 95% confidence level. The ideal situation has a statistically significant regression ( $p < 0.5$ ) and a larger  $r^2$  value ( $> 90\%$ ), and a small or statistically non-significantly intercept. The regression slope generated is then multiplied by the initial arbitrary flux value (usually  $100\mu\text{g m}^{-2}\text{sec}^{-1}$ ) to

generate a closer flux value to the sampled air concentrations. When the model is rerun using the new flux value the regression slope should be closer to one, giving an accurate measure of fumigant emission rate at that time period (Johnson et al 1999). This procedure should be done for each time period of sampling to monitor the change in flux over time.

To generate the average flux for a 24 hour period, sample intervals taken over the day period are used to estimate a time weighted averaged 24-hour flux by the following equation.:

$$\text{Weighted average} = ((T_a \times F_a) + (T_b \times F_b)) / (T_a + T_b)$$

$T_a$  = Time of first period

$F_a$  = flux rate for first period

$T_b$  = Time of second period

$F_b$  = flux rate for second period

Using this equation, daily or weekly time weighted averages may also be calculated.

### Differences between EPA's Fumigant Air Dispersion Models

There are three major computer model simulations approved by the EPA for air dispersion modeling, ISCST3, CALPUFF, and American Meteorological Society/Environmental Protection Agency Regulatory Model (AERMOD). Each of these models allows for three different types of sources, line (e.g. cars on a road), point (e.g. stack plumes), and area (e.g. landfills). The Industrial Source Complex: Short Term (ISCST3) is a Gaussian model used to model transport of materials away from a source by estimating the concentration at a downwind and crosswind distance depending upon the degree of mixing in the atmosphere, and atmospheric stability (Ross et al 1996, O'Malley 2004). Atmospheric stability is broken down into 6 classes called the Pasquill Stability Classes (PSC), ranging from very unstable, to stable. These stability classes are generally based upon air turbulence. Air turbulence, in general is

created by rising air. Warm air rises relative to the surrounding colder air and continues its upward movement until it cools to the ambient temperature. Ambient temperature gradients, a reduction or increase per thousand feet elevation determine the PSC classification. If the air at a higher altitude is warmer than that at a lower altitude an inversion is created, and vertical air movement is attenuated (Beychok 2005).

These PSC's can also be defined according to wind speed and insolation (incoming solar radiation). Generally as surface wind speed decreases, and as solar radiation increases, a less stable atmosphere is created. While temperature inversions are more common at night, they can and do occur during daylight hours. Stable atmospheric conditions that result in inversions don't allow the vertical dispersal of airborne material, in this case MITC, and tend to lead to higher measured ground-level concentrations when compared to less stable atmospheric conditions (Beychok 2005).

In 2006 the EPA chose AERMOD to replace ISC as its preferred dispersion model (Cimorelli et al. 2004). AERMOD is a probability density function (pdf) dispersion model that uses Gaussian dispersion during periods of stable weather conditions, switching to non Gaussian probability during unstable conditions. AERMOD is a much more complex model compared to ISC, allowing for several different weather data inputs.

ISC-AERMOD View is a graphical user interface (gui) version of ISC produced by Lakes Environmental Software, combining the ISC and AERMOD computer models, into one program. Users input data through a windows interface rather than writing the input files in standard ascii format.

CALPUFF from Earth Tech and Inc. is the newer Lagrangian Gaussian puff model program in use with the EPA which instead of plumes, focuses on puff modeling of emissions.

Puff modeling characterizes each data emission (sampling period) as a separate puff, able to transport and transform independently from other emission points. CALPUFF is generally thought to be superior for long range transport, and as good or better at short distance modeling than ISCST3 (Scire et al. 2000). CALPUFF can use multiple weather monitor stations to generate a 3-D model to more accurately determine the transport of airborne materials in the environment, including MITC.

CALPUFF is a very powerful model that is capable of looking at long distance transport of materials. Most agricultural fields are located in rural areas, where few structures impacting the air transport of materials from the edge of the field to the location of air samplers. Because most users are interested in the distance between the field and the air monitoring receptor stations, CALPUFF is not the model of choice. It would be excellent at looking into potential long range effects once flux values have been generated.

Wang et al (2006) compared the ISCST3 model to CALPUFF based upon modeled air odor detection. The ISCST3 model tended to show lower levels of odor detection that were actually measured. The CALPUFF model was good at predicting downwind odor levels, and both models had difficulties predicting the highest concentrations. Back calculated flux levels were statistically different for each computer model, indicating each set of estimates were model specific (Wang et al. 2006).

Relying on emission concentrations generated in the previous mentioned models, the Probabilistic Exposure and Risk Model for FUMigants (PERFUM) has been used by the EPA to determine risk factors and potential buffer zones based upon human inhalation exposure assessments (Sullivan et al. 2004a, Sullivan et al 2004b, Reiss and Griffin 2006). Buffer zones are set-back distances around the field of application to protect bystanders from fumigant

exposure during and post-application. For fumigants, buffer zones have been specified by the EPA based on application practice, rate of application, and size of the field (US EPA 2008). The output data can be generated in PERFUM in accordance with whole field averaged emissions or using a maximum emissions approach. The whole field approach generates a buffer so that a large portion of the perimeter has a maximum exposure limit or margin of exposure (MOE) greater than or equal to the target. The margin of exposure is defined as the ratio of NOAEL to the estimated exposure dose. The maximum concentration approach generates a buffer zone around the field producing the emissions, so that no part of the buffer will be above the MOE. The maximum concentration approach will generally generate larger buffer zones than the whole field approach, making it the more restrictive/protective of the two approaches. PERFUM uses the same program engine as ISC, making the two programs very compatible.

#### Factors Influencing Fumigant Flux

Flux of MITC from soils is influenced by several different factors including the rate of diffusion between the soil/water and the atmosphere. This process is controlled by several factors including; pesticide vapor pressure, soil adsorption coefficient, and water solubility (Dungan et al 2003). Factors contributing to flux can be influenced by making changes in agricultural practices including application rate, and depth of soil incorporation/application, soil moisture levels, and soil/air temperature. Understanding how these potential changes influence the flux of MITC is critical to reducing downwind concentrations, and thereby possible exposures.

The type of ground application will have a direct effect on the depth of application and subsequent surface fumigant emissions. Metam is generally applied in potato fields via two

main practices, surface “water run” application by center pivot chemigation (with or without low drizzle boom, with or without end gun), and soil incorporated shank injection (with or without tarp). Metam can also be applied by drip-line with or without tarp for row crops such as strawberries (Papiernik et al 2004b, Li et al 2006) but this technology is generally not used in large field scale potato production due to the prohibitive cost of tarping entire fields (approximately \$270 per acre compared to \$15 per acre for metam applications via sprinkler application, \$45 for shank injection) (Goodhue et al 2003, Hinman et al 2001, Hinman et al 2006). In the Pacific Northwest, especially in the Columbia Basin, center pivot chemigation has been historically used. Due to the dry nature of the climate, the region is predominately irrigated via center pivot. Besides access, center pivot application has many other benefits including reduced cost, and a decreased risk for exposure for applicators since they need only be nearby during fumigant application. Shank injection has not become popular due to the higher cost of application (Hinman et al 2006), mainly in fuel, man hours and equipment.

Shank injection applies the material within the soil to a depth of 5-20cm, but center pivot chemigation applies the material on the surface. Drip line applications are buried in rows up to 30cm in depth (Papiernik et al 2004b). Surface fumigant applications are anticipated to be transported deeper into the soil via water transport. Studies (Saeed et al 2000, Sullivan et al 2004a, Wofford 2005, Wofford et al 2005, Zheng et al 2006) have shown that shank injection can substantially decrease the emission rates compared to chemigation. Reported percentage of total loss estimates from volatization for shank injection vary greatly, ranging from 6% (Sullivan et al 2004a), 14% (Wofford et al 2005) to 36-38% (Sullivan et al 2004a, Zheng et al 2005). Similarly, chemigation application percentage of total loss estimates differ, ranging from 13% (Sullivan et al 2004), to 63% (Sullivan et al 2004a) to 88% (Wofford 2005, Zheng et al 2005).

Use of a water seal post application for shank injection can reduce total losses significantly (38% to 13%) (Zheng et al 2005). Estimated losses for both chemigation and shank injection vary greatly from experiment to experiment depending upon environmental factors (season of application, differences in soil) and additional watering practices. Papiernik et al (2004a) also showed that increasing the depth of application in drip-line application from 15 to 30 cm reduced pesticide flux from 8.2 to 2.7  $\mu\text{g m}^{-1} \text{s}^{-1}$ . Increased depth of application also increased the amount of time from initial application to peak flux from 3-7 hours up to 26-52 hours, leading to a decrease in magnitude of flux by 70%; use of a tarp further reduced the emissions. Zheng et al (2006) showed that MITC stayed deeper in the soil profile when applied with shank injection than with standard chemigation.

Incorporation of outside organic material has also been shown to decrease total surface MITC emissions by increasing the rate of degradation of MITC. Gan et al (1998) added either composted steer manure (CM) or bio-solids (BM) to a reference soil to measure possible enhancement of MITC degradation. Adding a 1:20 (5%) ratio of CM to soil reduced MITC degradation half-lives from 3.4 days to 0.4 days. The results were not as compelling for BM. They further demonstrated that volatilization was decreased greater than 10-fold when a 5% CM addition was mixed into the top 5cm of the soil. Dungan et al (2003) reported that chicken manure can have similar effects on enhanced degradation and MITC soil retention. Conversely, the increase in degradation may have an adverse impact on effectiveness of applications. Gerstl et al (1977) found that peat moss (95% organic material) had no detectable levels of MITC after 30 min, compared to soils low in organic material. Sterilized soil had a slower degradation rate, regardless of temperature or organic content, indicating the importance of microbes on

breakdown of MITC (Zheng et al 2007). Repeated applications, less than 3 years apart, increased degradation of MITC, compared to similar virgin soils (Triky-Dotan et al 2007).

Soil temperature can have a large impact on conversion of metam-sodium to MITC, MITC degradation and ultimately emission rates. In soils with high temperature and low moisture levels, metam-sodium degrades to MITC at a faster rate (Gerstl et al 1977, Zheng et al 2006). If MITC is degraded in the soil before it can volatilize, emission rates should be lower (Dungan et al 2003). Dungan et al (2003) and Gan et al (1999) both showed that increases in soil temperature caused an increase in degradation of MITC. Half life of MITC decreased from 5.8 days at 20<sup>0</sup>C, to 3 days at 30<sup>0</sup>C and 1.8 days at 40<sup>0</sup>C in unamended soil (Dungan et al 2003). The chicken manure augmented soils showed similar decreases in half lives as the temperature increased. Gan et al (1999) reported similar reductions as temperature increased. Applications under cooler conditions have also been shown to decrease emissions (Van Den berg et al 1999), with estimated total losses of 34% in October, and 17% in November. Increased soil/air temperature increases the vapor pressure between the soil/water and the atmosphere, causing emissions of MITC to increase (Li et al 2006). The combination of high vapor pressure and low water solubility of MITC indicates the propensity of movement from soil to the atmosphere, especially as temperature increases. Flux of MITC has been shown to decrease during nocturnal periods of sampling (i.e. cooler temperatures), indicating this may be the case (Li et al 2006).

Soil moisture and irrigation technique can have a large impact on MITC emission rates. MITC moves through the soil through gas diffusion, and can be greatly inhibited by moisture. Sullivan et al (2004) reported that the addition of a post application water seal for both shank and chemigation reduced emissions when compared to no water seal. Zhang et al (2007) observed that the addition of pre with post irrigation waters caused a dramatic reduction in surface

emissions, even compared with tarp alone or tarp with partial water seal. Using a chamber experimental model, these investigators demonstrated that a tarp with no irrigation had a MITC flux of  $56.5\mu\text{g cm}^{-2}\text{ hour}^{-1}$ . When compared with tarpaulin and pre application water seal, the emission rate was reduced to  $35\mu\text{g cm}^{-2}\text{ hour}^{-1}$ . Pre application and post application watering greatly attenuated flux to  $0.3\mu\text{g cm}^{-2}\text{ hour}^{-1}$ . Zhang et al also observed that MITC remained deep (30-50 cm) in the soil for a longer period with a post application water seal compared to pre irrigation or no irrigation. They also note that heavy post application irrigation can possibly result in leaching and present concerns for areas with shallow water tables. Zheng et al (2006) reports that formation of MITC from metam-sodium was delayed as soil moisture levels increased. In laboratory experiments increasing the moisture levels from 10% to 20 and 30% slowed the total conversion from 10 min to 20 and 30 min respectively. Increasing moisture content also had the effect of lowering both the rates, and the total amount of MITC emissions.

Soil moisture levels can also have an influence on both metam-sodium and MITC degradation. Dungan et al (2003) demonstrated that increasing soil moisture content had a negative effect on MITC degradation. The half life of MITC in soil was increased from 4.3 days to 5.8 days, by doubling soil moisture levels from 25% to 50%. Results from Gan et al (1999) showed a similar trend. Conversion of metam-sodium into MITC is also dependant upon soil moisture levels. Degradation of metam into MITC decreased 4 fold by increasing soil/water ratio from 1:0.15 (8 min) to 1:1 (32 min) and 1:10 (120 min); using  $640\mu\text{g metam-sodium g}^{-1}$  soil at  $20^{\circ}\text{C}$ . Using a lower concentration of  $48\mu\text{g g}^{-1}$  showed greater discrepancy, <1min and 40 min respectively for the two lowest soil/water ratios (1:0.15 and 1:1). A higher concentration of  $3200\mu\text{g g}^{-1}$  only indicated an increase at the highest soil/water ratio 41 minutes to 126 minutes (1:10) (Gerstl et al 1977).

Barriers placed on the soil immediately following application have been shown to reduce emissions of fumigants. In a soil studied under both laboratory and field conditions virtually impermeable films (VIF) placed over the application areas reduced cumulative emissions to 0.005% compared to emissions of 1.6% from 1-mil high density polyethylene (HDPE) (Papeirnik et al 2004b). Physical barrier polymers are applied directly following shank injection with the edges of the tarp buried on each side using field equipment. They can also be applied when forming the rows, when the application will be from by drip irrigation lines. VIF and HDPE barriers are generally not used in potatoes due to both increased cost of materials and removal (approximately \$526 acre<sup>-1</sup> and \$100 acre<sup>-1</sup> respectively in addition to fumigant costs in California) (Gao et al 2008)

### **C. CONCLUSION**

Metam-sodium is a valuable chemical for growers, providing an excellent means of controlling target pests. Due to its chemical nature (i.e. low water solubility and high vapor pressure) it has the potential to transport offsite and impact nearby residential communities in a harmful manner. Accidental exposures in California and recently measured MITC concentrations in air of residential areas in Washington State indicate the potential for future exposures. These incidents have prompted the EPA to consider new guidelines for metam-sodium applications. Understanding the interactions of environmental factors impacting the potential for flux of MITC is critical for reducing off site transmission.

Factors influencing flux of MITC include application method/rate/depth, air/soil temperature, soil moisture levels, and soil composition. Comparing flux values of MITC from different field studies becomes problematic due to the number of variables that can influence

flux. Flux information generated under summer conditions may not be representative of applications done under cooler fall conditions due to the influence of temperature on both metam-sodium/MITC degradation, and increased potential for MITC to volatilize.

While there are many ways to measure field flux values for fumigants such as MITC, one of the simplest is the aerodynamic method combined with computer modeling to “back-calculate” values. This method accommodates any field size and shape, and requires less equipment than other methods. It has been successfully used by both CAL DPR and EPA to generate flux information on several fumigants including metam-sodium.

Studies using field applications to generate flux information, especially those comparing different application techniques should limit as many variables of flux as possible. One consideration is to use a single field, with simultaneous applications to limit differences in soil composition and air/soil temperature. Soil moisture levels may differ depending upon the application method used (drip line irrigation and center pivot chemigation versus shank injection). Information generated from this type of study could provide valuable information on the effect of application methods on resulting flux of MITC. Reducing exposure to MITC while still maintaining availability of metam-sodium for growers should be a priority. If changes in agricultural application processes will allow both to occur they should be encouraged.

Table 1.1. Characteristics of Metam-Sodium

Common Names:	Metam-sodium, Metam, Metham, Metham-sodium, Carbathion.
Chemical Names:	Methyldithiocarbamic acid sodium salt; methylcarbamodithioic acid sodium salt; sodium methyldithiocarbamate.
Formulation Types:	Soluble liquid concentrated, aqueous solutions.
Some Trade Names:	Vaporoooter® and Vaporoooter®II (A Irrigation Engineering Co., Inc.), Amvac® Metam and Metam 426 (Amvac Chemical Corp.), Busan™1016, Busan™1020, and Busan™1236 (Buckman Laboratories, Inc.), Polefume® and Vapam® (ICI Americas, Inc.), Nalco 08964 (Nalco Chemical Co.), Sectagon II® (Oregon-California Chemicals Inc.), and Woodfume® (Osrose Wood Preserving, Inc.).
CAS Registry Number:	137-42-8
Molecular Formula:	C <sub>2</sub> H <sub>4</sub> NNaS <sub>2</sub>
Molecular Weight:	129.2 (Tomlin, 1997).
Physical Form:	Colorless crystalline dihydrate (Tomlin, 1997).
Vapor Pressure:	Non-volatile (Tomlin, 1997).
Solubility:	Water: 9.63 x 10 <sup>4</sup> ppm (at 25 °C) DPR, 1999). 7.22 x 10 <sup>5</sup> ppm (at 20 °C) (Tomlin, 1997). Practically insoluble in most other organic solvents (Tomlin, 1997).
Density:	1.1648 g/mL at 20 °C (Myers, 1985).
Aqueous Photolysis Half-life:	3.75 x 10 <sup>-2</sup> day (pH 7; 25 °C (DPR, 1999)
Hydrolysis Half-life:	4.85 days (pH 7; 25 °C) (DPR, 1999).
Anaerobic Soil Metabolism Half-life:	<1 day (pH 7.9; sandy soil) (DPR, 1999).
Aerobic Soil Metabolism Half-life:	1.6 x 10 <sup>-2</sup> day (pH 6.9; sandy soil) (DPR, 1999).
Field Dissipation Half-life:	2.54 days (pH 6.3; loamy soil) (DPR, 1999). 4.00 days (pH 7.5; sandy loam soil) (DPR, 1999).
Stability:	Stable in concentrated aqueous solution, but unstable when diluted. Decomposition promoted by acids and heavy-metal salts (Tomlin, 1997).
Degradation and Metabolism:	In soil, rapidly decomposes to methyl isothiocyanate, which is volatile and quickly evaporates (Tomlin, 1997).

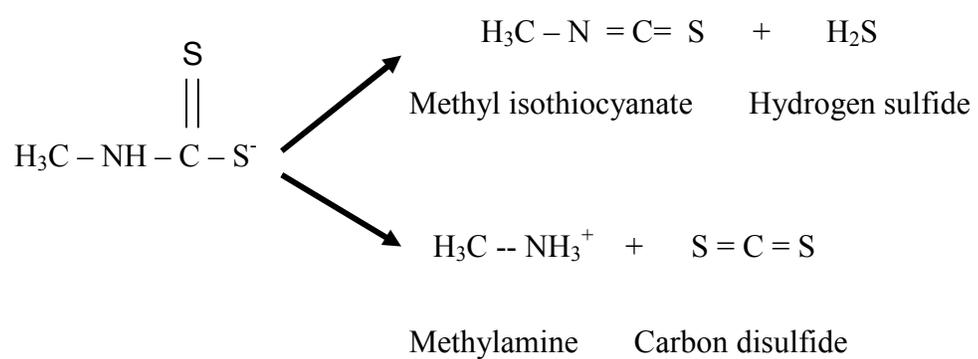
Table 1.1 Taken from Rubin 2002

Table 1.2. Characteristics of Methyl Isothiocyanate

Common Names:	Methyl isothiocyanate, MITC, MIT, methyl mustard oil.
Chemical Names:	Methyl isothiocyanate, Isothiocyanatomethane.
Formulation Types:	Emulsifiable concentrate.
Some Trade Names:	Degussa MITC (Degussa Chemical Company). MITC-Fume® (Osmose Wood Preserving, Inc).
CAS Registry Number:	556-61-6
Molecular Formula:	C <sub>2</sub> H <sub>3</sub> NS
Molecular Weight:	73.1 (Tomlin, 1997).
Physical Form:	Colorless crystals with a horseradish-like odor.
Vapor Pressure:	16.0 mmHg (25 °C) (DPR 1999). 16.0 mmHg (25 °C) (Tomlin 1997). 20.3 mmHg (20 °C) (Leistra and Crum 1990). 19.5 mmHg (20 °C) (Degussa 1988).
Solubility: Water:	8.23 x 10 <sup>3</sup> ppm (20 °C) (DPR 1999). 8.61 x 10 <sup>3</sup> ppm (25 °C) (DPR 1999). 8.2 x 10 <sup>3</sup> ppm (20 °C) (Tomlin 1997). Readily soluble in common organic solvents, such as ethanol, methanol, acetone, cyclohexanone, dichloromethane, chloroform, carbon tetrachloride, benzene, xylene, petroleum ether, and mineral oils (Tomlin1997).
Octanol/Water Partition Coefficient (K <sub>ow</sub> ):	15.8 (DPR 1999). 23.5 (Tomlin 1997).
Henry's Law Constant:	1.79 x 10 <sup>-4</sup> atm×m <sup>3</sup> /mol (25 °C) (DPR, 1999). 2.4 x 10 <sup>-4</sup> atm×m <sup>3</sup> /mol (20 °C) (Montgomery, J.H 1997). 2.66 x 10 <sup>-4</sup> atm×m <sup>3</sup> /mol (20 °C) (Geddes et al 1995).
Specific Density:	1.048 g/cm <sup>3</sup> (24°C), with respect to water at 4 °C (Tomlin, 1997).
Aqueous Photolysis Half-life:	51.6 days (pH 7; 23 °C) (DPR, 1999).
Hydrolysis Half-life:	20.4 days (pH 7; 25 °C) (DPR, 1999).
Stability:	Unstable and reactive. Rapidly hydrolyzed by alkalis, more slowly in acidic and neutral solutions. Sensitive to oxygen and to light (Tomlin 1997).
Degradation and Metabolism:	In moist soil, degradation and evaporation of the bulk of the substance occurred within 3 weeks at 18-20 °C soil temperature, 4 weeks at 6-12 °C, and 8 weeks at 0-6 °C (Tomlin 1997).

Table 1.2. Taken from Rubin 2002

Figure 1.1 Chemical Conversion of Metam sodium to MITC (from Pruett et al 2001)



## CHAPTER 2

# Estimating Methyl Isothiocyanate Emission Rates following Soil Incorporated Shank Injection and Modified Center Pivot Fumigation

### Introduction

Growers rely on the thiocarbamate fumigant metam sodium/potassium (trade names Vapam, Sectagon, Busan, and Metam CLR/KLR), as a pre-plant soil fumigant to reduce the incidence of early die caused by *Verticillium* spp. Without the use of metam, this organism can significantly reduce quality and yield. Applications are typically performed by center pivot chemigation in the fall at a rate of ca. 170 lbs active ingredient per acre (i.e., 40 gallons of 40% metam per acre). Besides *Verticillium*, this product can be effective in controlling other soil-borne plant pathogenic organisms including certain soil surface nematode populations and various weeds. Reliance on this fumigant is largely a result of its effectiveness for soil-borne pathogen control and low cost of application. Metam sodium quickly converts to its acting agent methyl isothiocyanate (MITC) in the presence of water after application. MITC volatilizes from the soil into the atmosphere, and can be accidentally transported away from the application site on wind currents (O'Malley et al 2004, WSU FEQL 2006, LePage and Hebert 2008). Especially in the Pacific Northwest (PNW), rapidly expanding residential growth into traditionally agricultural areas has caused the US Environmental Protection Agency (US EPA) to consider new buffer zones for metam applications to both reduce by stander exposure and maintain public safety (US EPA 2008).

Starting in 2005, metam sodium along with other methylthiocarbamate salts underwent a reregistration review overseen by EPA Office of Pesticide Programs (EPA-OPP or Agency) leading to a July 2008 reregistration 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 (Sullivan 2004). Information on near field MITC concentrations in California done under spring and summer conditions has been well documented (CEPA 1993, CEPA 1994, Wofford et al 1994, CEPA 1997, Wofford 2005, Wofford et al 2005, Wofford 2007). Whole field and flux studies of MITC specific to the Pacific Northwest's cooler fall season application conditions are limited and 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. 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, mainly spring and summer. 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 in the PNW exist in close proximity to residential communities, strict adherence to the current RED buffer zone criteria could have serious economic implications. The majority of applications done in the PNW are by center pivot chemigation, due to decreased costs. Generation of flux values for metam applications under conditions for the PNW is vital for both growers and regulators both for bystander safety but also to keep product where it will be the most effective, in the soil.

Flux of MITC and other fumigants is influenced by several factors including soil

composition (Gerstl et al 1977, Gan et al 1998, Di Primo et al 2003, Dungan et al 2003), soil moisture levels (Dungan et al. 2003, Sullivan et al 2004, Zheng et al 2006, Zhang et al 2007), depth of application (Saeed et al 2000, Papiernik et al 2004, Sullivan et al 2004), and soil temperature (Gan et al 1999, Van de Berg et al 1999, Ma et al 2001, Dungan et al 2003). In order to fully compare the influence of application methods on flux, they should be done under similar if not identical conditions, i.e. concurrently on a single field.

The US EPA's Gaussian plume dispersion model, Industrial Source Complex (ISC) has been used to "back calculate" flux values for several chemicals including methyl bromide and methyl isothiocyanate (Wofford et al 1994, Johnson et al 1999, Ross et al 1999, Li et al 2006). ISC has been the computer model of choice due to the proportional relationship between flux and air concentration by using a computer model of the field and air samplers, measured near field air concentrations and onsite weather conditions to create a reasonable approximation of flux. This approach allowed the use of smaller field plots to represent whole field applications, allowing us to directly examine the influence of shank injection with roller compaction versus drizzle boom modified center pivot chemigation on flux of MITC under conditions seen by PNW growers, while minimizing the influence of outside factors, something not possible on separate fields.

## Materials and Methods

### Drizzle boom modified center pivot chemigation

The ca. 2-acre drizzle boom and shank test plots were positioned within a single 122-acre, eight tower center pivot circle in Franklin County, WA. The field was disc plowed and watered prior to fumigant application. The test plots were positioned at these northwesterly and

southeasterly locations to minimize MITC cross contamination from anticipated southwesterly prevailing winds over the study time frame (Figure 2.1). Three days prior to application the air samplers and weather station were setup, and exact locations were recorded via GPS. Sectagon 42<sup>®</sup> was applied to a ca. 1.7 acre plot section, slightly less than then initially anticipated. Center pivot towers 1-3 and 8 were capped off during this trial and towers 4 through 6 were modified for low drift drizzle boom attachment. This horizontal boom constructed of PVC piping was attached to existing sprinkler heads allowing application 2-3 feet from the soil surface. Sectagon 42 was applied with 1 inch of water to set the product within the soil. The start and stop times for this application were respectively 11:35 am and 1:30 pm, October 9, 2008. A total of 120 gallons of Sectagon 42 was applied over this 1 hour 55 minute application period, representing a 71 gal acre<sup>-1</sup> application. Both applications were to be made at ca. 50 gal acre<sup>-1</sup> but due to an error calculating in area the drizzle boom field plot was applied at a greater rate.

#### Soil-incorporated shank injection

On October 9<sup>th</sup>, 2008 starting at 12:10 pm, Sectagon 42<sup>®</sup> was applied at a rate of 52 gal acre<sup>-1</sup> to a 1.8 acre field plot by shank injection at a ca. depth of 9 inches followed by soil compaction. The application took place during a 40 min time frame using a total of 93 gallons of product. This test plot was “double disc plowed” before application to allow uniform penetration of the blades to the required depth. Shank injection application was started at a later time based on estimated application time to have both applications end near the same time to coincide post application sampling intervals.

## Near field air monitoring stations

The eight receptors at each field plot were positioned ca. equidistantly and ca. 15 meters from the treated edge (Figure 2.1). Four additional ambient air receptors were positioned between the two treatment plots, one near the center of the center pivot circle, one near the southwest circle field corner and two near equidistant between the drizzle boom and shank injection plot (Figure 2.1). These additional receptor sites were included to evaluate potential contribution of off-target MITC emissions over the experimental time frame. Two sampler locations per field site had duplicate samplers to assess site specific emission variation. MITC in ambient air was monitored pre-application, during fumigation and at either 4 or 8 hour periods through 4 days post-application. Each receptor location consisted of an SKC personal air sampling unit (SKC Model PCXR4) placed at the base of a sampling mast in a protective case, with a vertical ca. 1.5-meter height crossbar. 600 mg charcoal-filled cartridges (SKC # 226-09) were located at the end of the crossbar. Each receptor unit over the study time frame was powered by DC current via marine battery. Air flows, set at  $1\pm 0.1$  L/min, were measured and recorded at the start and end of collections. Flow rates were averaged over each sampling interval using the beginning and end flow rate. Upon collection, cartridge samples were capped and stored on dry ice until transfer to  $-80^{\circ}\text{C}$  freezer at Food and Environmental Quality Laboratory (FEQL) until analysis.

### Onsite weather stations

Two in-field weather collection devices collected meteorological information prior and over the experimental time frame. Wind speed/direction, air/soil temperature, soil moisture and rainfall-weather information were collected by a HOBO Weather Station data logger<sup>®</sup> system. Wind speed and direction were recorded at a 2 m height. Soil temperature and soil moisture levels were recorded at 6” depth. The weather station was located in the center of the field north of the shank injection plot and east of the drizzle boom field. A CSAT3 3-D sonic anemometer maintained by Sullivan Environmental Consulting Inc was also employed to collect wind speed/directional data at 3 m height. Both weather data systems collected on a 1 minute basis and were averaged to one hour for use in computer modeling.

### Analytical method

The analytical method for the solvent extraction of MITC from activated charcoal cartridges and subsequent air concentration determination followed a previous method reported by LePage and Hebert (2008), originally modified from the California Department of Pesticide Regulations solvent extraction method (Cal DPR 1994). Sample charcoal was extracted using 5 ml of 20% carbon disulfide, 80% ethyl acetate on ice and then briefly sonicated, then filtered using a 0.45µl syringe filter into a GC vial. The extracted solvent was injected into a Varian Star 3400CX gas chromatograph with nitrogen-phosphorus specific detection equipped with a Alltech EC-WAX, 15m x 0.53mm, 1.20µm film thickness column. Helium was used as the carrier gas with a column flow rate of ca 3.5 mL min<sup>-1</sup> at 55 °C. Injector temperature was 55 °C to 225°C

(rate:  $225^{\circ}\text{C min}^{-1}$ ), hold 5 min. The oven temperature was set  $55^{\circ}\text{C}$ , hold for 0.09 min, ramped at  $10^{\circ}\text{C min}^{-1}$  to  $90^{\circ}\text{C}$ , holding for 5 min. The method was validated in triplicate at  $0.25\mu\text{g}$  MITC to establish a limit of quantitation (LOQ). The method LOQ for air samples was established at 70% of the lower limit of method validation ( $0.25\mu\text{g}$  total MITC) or approximately  $0.36\mu\text{g m}^{-3}$  based on  $1\text{ L min}^{-1}$  air flow for 8 hr sampling interval ( $\sim 0.48\text{ m}^3$  air sampled). The limit of detection (LOD) was estimated to be approximately one-fifth of this value or  $0.07\mu\text{g m}^{-3}$  based on  $1\text{ L min}^{-1}$  air flow for 8 hr sampling interval ( $\sim 0.48\text{ m}^3$  air sampled). The method was also validated at  $25\mu\text{g}$ , and  $300\mu\text{g}$  MITC to encompass anticipated concentration levels. Average method validation recovery was  $97.8 \pm 5.6\%$  ( $n=9$ ). Analytical standards bracketed no more than three samples. Each set of samples were extracted with at least two concurrent fortified samples and one non-fortified activated charcoal sample. Average concurrent fortified sample recovery was  $95 \pm 9\%$  ( $n=95$ ). All samples were stored at  $-80^{\circ}\text{C}$  until extracted, and all samples were extracted within 60 days from collection, well within a previous 80 day storage stability study (data not shown).

### Quality control samples

Field fortifications (together with their associated control blank cartridges) were performed to verify quantitative retention of the MITC on the activated charcoal over the longest period of air sampling. The average MITC recovery from field fortifications was  $94 \pm 2.7\%$  ( $n=3$ ). Additionally, fortified trip samples were used to ensure integrity from the field through laboratory frozen storage, to chemical analysis. Cartridges were spiked with  $100\mu\text{g}$  MITC and transported to the field during sample intervals, and were returned with the field samples to

FEQL to simulate handling of the air monitoring samples. The average recovery from the 600 mg fortified trip blanks was  $95 \pm 3.5\%$  (n=5). Non fortified cartridges were also transported with the field samples with no MITC was detected on those samples (n=4).

### MITC field emission rate estimations

To assess the potential for bystander exposure in a manner consistent with practices employed by regulatory agencies and registrants, MITC volatilization density (flux) in units mass surface area<sup>-2</sup> time<sup>-1</sup> together with total cumulative emission loss over the 5-day fumigation/post fumigation period were estimated by a back calculation approach from the collected receptor emission and gathered meteorological data according to procedures from Johnson et al (1999) and Ross et al (1999). GPS Coordinates were converted into Cartesian coordinates for each corner of the individual field plots and near field air samplers (Figure 2.1). The ISC portion of ISC-AERMOD View© (Lakes Environmental Software) was used to generate the computer model of the field using the generated coordinates (Figure 2.1). Weather data collected by the onsite HOBO Pro weather station was averaged into one hour intervals using HOBOware Pro software. 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. Each field plot was modeled individually with an initial flux value of  $1\mu\text{g m}^{-2} \text{sec}^{-1}$ . Emission estimations were particularly considered reliable if measured and modeled linear emission estimates were strongly associated (i.e., >0.95). If so, the linear regression slope served as the emission rate estimate. If the least squares slope without an intercept was not significant at the 95<sup>th</sup> percent confidence level, then the more conservative

mean measured divided by the mean modeled emissions rate was used to calculate the emission rate for that period. This practice was needed for shank injection emission rate calculations primarily during the first six sampling intervals due to interference from the upwind drizzle boom field plot. Sample intervals for the first 20 hours showing high concentrations from upwind sources impacting the downwind air samplers were evaluated for the potential of upwind subtraction according to CDPR protocol (Wofford and Johnson 2006) (Figure 2.2). For periods of significant contribution from one field plot to another, mainly the first six sampling intervals, downwind concentrations generated using the generated flux value were subtracted from measured concentration before evaluation. This least-squares technique regressed field-measured to model-predicted emissions over the 4-day experimental timeframe. Total losses for the four day sampling interval were generated by summation of the multiplying the flux value (F) for a given interval by the sampling time (T) divided by the application rate per square meter (A).

$$((F_1 * T_1) + (F_2 * T_2) \dots (F_{20} * T_{20})) / A$$

## Results

### Weather Data

Average air temperature over the sampling interval was 7.7°C (45.9 °F) with a high of 18.9°C (66 °F) and a low below freezing (-1.5°C or 29.3°F). Average 6” depth soil temperature during the trial was 10.2 °C (50.4 °F), with a high of 15.7 °C (60.3°F) and a low of 6.2 °C (43.2°F). The measured soil moisture level (at 6” depth) dropped from 1.41 to 0.094 VWC (m<sup>3</sup> water m<sup>-3</sup> soil) by the end of the sampling period. No measurable rainfall was recorded.

### Field-measured MITC emissions

Averaged concentrations were calculated using the average MITC concentration from the eight air sampling receptors per interval sampling period over the 4-day study (Table 2.1). Averaged whole field concentrations peaked during the 4-hours post application for drizzle boom modified center-pivot chemigation ( $417\mu\text{g m}^{-3}$  (138 ppb)) with a maximum single observation near-field concentration during this time of  $963\mu\text{g m}^{-3}$  (318 ppb). Maximum whole field-averaged MITC concentrations of  $78\mu\text{g m}^{-3}$  (26 ppb) were observed 16-hours post application for the shank treated field with a maximum single observation near-field concentration of  $122\mu\text{g m}^{-3}$  (40 ppb) registered during this same 16-20 hour receptor period. 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, indicating cross contamination from the drizzle boom field onto the shank injection near field samplers (Figure 2.3 and 2.4). Although all attempts were made to position test plots to minimize cross-contamination, it is reasonable to state that directional MITC drizzle boom source emissions contributed to the measured shank emission estimates, especially during the first 20 hours of this field demonstration. Standard deviation of MITC concentrations between duplicate samplers was less than 10%.

### Drizzle boom

Computer modeling of flux for the drizzle boom field plot generally conformed to the actual measured near field air MITC concentrations. During one interval (Period 4) strong variations in wind speed and direction resulted in poor relation and the more conservative mean measured/mean modeled method was used to determine emissions. Flux was highest during

application ( $171\mu\text{g m}^{-2}\text{ sec}^{-1}$ ) and for the first 4 hour period post application ( $206\mu\text{g m}^{-2}\text{ sec}^{-1}$ ). Flux decreased slowly to  $32.2\mu\text{g m}^{-2}\text{ sec}^{-1}$  at 24 hours post application and  $15\mu\text{g m}^{-2}\text{ sec}^{-1}$  48 hours post application (Figure 2.5). Time weighted average MITC flux over four days was  $24.6\mu\text{g m}^{-2}\text{ sec}^{-1}$ . Cross contamination from the shank field was minimal. Following the technical procedures outline by Cal DPR's emission estimation process, the estimated total cumulative MITC loss by drizzle boom was calculated to be ca. 45% (total cumulative loss here assumes a 1:1 molar stoichiometry, complete conversion of metam sodium to MITC, and loss is by surface emission after application).

#### Soil incorporated shank injection

In contrast to the drizzle boom field, movement of air borne MITC from the drizzle boom field plot interfered with shank injection plot during the five of the first six sampling intervals, including application. Winds predominately from the northwest (Figure 2.2) combined with low emissions from the shank field showed little conformity when calculating flux with the ISC computer model during the first six sampling intervals. Subtracting modeled estimates from the drizzle boom field using the intervals flux value, improved the linearity slightly and did result in appreciably lower flux values than the standard mean measured/mean modeled approach, 2.2 versus  $8.1\mu\text{g m}^{-2}\text{ sec}^{-1}$  during application. During these first intervals reliance on the more conservative mean modeled/mean measured estimates was required even after subtraction of upwind contributions. During later sampling intervals wind direction did not indicate cross contamination from the drizzle boom field onto the shank field. Flux values for the shank injection field plot were highest during these five intervals (maximum  $12.6\mu\text{g m}^{-2}\text{ sec}^{-1}$ ) compared to later intervals (maximum  $8.2\mu\text{g m}^{-2}\text{ sec}^{-1}$ ) (Figure 2.6). Time weighted flux values

for the 4 day trial are  $3.2\mu\text{g m}^{-2}\text{ sec}^{-1}$ , with total losses of MITC over the four day sampling period were determined to be ca. 8% by soil incorporated shank injection

## Discussion

Application of metam sodium by shank injection resulted in lower TWA receptor air MITC concentrations than drizzle boom by almost ten fold during, and greater than five-fold post application for the first three days. The highest drizzle boom receptor air concentrations occurred during application (263 ppb) and the first four hours post-application (317 ppb), compared to sixteen hours post application for shank injection (40 ppb). Computer model predictions of flux provided good linearity between predicted and actual measured air concentrations when wind direction was consistent over the hourly period. Periods of drastic changes in wind direction within the hourly period show the limitations of the ISC computer model. During the first six sampling periods post application, wind direction was generally from the northwest causing airborne MITC to move from the drizzle boom field onto the shank field (Figure 2.2). This can be seen in the gradient of MITC from high concentrations of near field MITC detected on the south drizzle boom air samplers, the two ambient air samplers between the two field and the near field air samplers on the north side of the shank field (Figure 2.3, 2.4). Cross contamination from the drizzle boom field onto the shank field during these periods created difficulty in determination of estimated flux. Subtraction of the upwind concentrations of MITC using CDPR procedures was only slightly successful in alignment but did result in lower emission rates. When defaulting to more conservative approach for periods where measured field emissions do not fit modeled prediction, it is reasonable to anticipate over-estimation of field emission rates. This may especially be prevalent under circumstances where

higher near-field source contributions can mask actual field emissions from lower emission applications such as shank. Background MITC from other regional applications also created interference with back calculation of flux of MITC for this study similar to previous field studies (CEPA 1994, CEPA 1997). Low concentrations of near field MITC were detected in air samplers where the model predicted there would be none, possibly the result of background MITC from nearby regional applications. Pre-application near field air samples as well as concurrent field fortification samples at FEQL all detected ambient MITC from other applications at low levels (up to  $14.3\mu\text{g m}^{-3}$  in an 8-hour sample). Since late October is a typical time for PNW growers to make metam sodium applications and MITC has been shown to travel long distances from the application site (greater than 1 mile) (O'Malley et. al 2004) avoidance of background MITC is unpractical.

Flux of MITC for drizzle boom modified center pivot chemigation was strongly correlated with increases in both soil and air temperature on both the second and third day post application (Figure 2.5). Flux values almost doubled both days  $26 - 57\mu\text{g m}^{-2}\text{sec}^{-1}$  on 10/10/09 and  $15-31\mu\text{g m}^{-2}\text{sec}^{-1}$  on 10/11/09. Increases in air temperature were similar for both days during this time period,  $3^{\circ}\text{C}$  at 8 am to  $14^{\circ}\text{C}$  at 3pm. Increases in soil temperature were similar for both days as well,  $8^{\circ}\text{C}$  at 8 am to  $12^{\circ}\text{C}$  at 3pm. This is similar to other studies that have shown a strong correlation between increases in air/soil temperature and emissions of MITC (Gan et al 1999, Van de Berg et al 1999, Ma et al 2001, Dungan et al 2003). Flux of MITC for shank injection did not show a strong increase during these periods.

This field-scale 2008 reduced-emission application information provides regionally specific emission flux data typical of the cooler fall climatic conditions when PNW fumigations are occurring. Although emission flux was back-calculated using measured air concentrations

based upon approximately 2-acre field plots, flux terms generated for this field-scale emission demonstration should be representative of field emissions from 100-200 acre field applications that typify this region. Near-field measured emissions from earlier larger field MITC bystander evaluations conducted in 2007 are complementary to observed emissions. Based on our findings, we anticipate that appreciable reductions can be realized in fumigant emissions through grower/consulting agronomist adoption of reduced emission practices especially shank injection over the more traditional center pivot chemigation even when modified by drizzle boom.

## CHAPTER 3

### FINAL CONCLUSIONS AND FUTURE WORK

The emission and flux evaluations from this field-scale study show that shank injection should be the preferred method for application of metam sodium, especially near residential areas. The lower measured near field air concentrations suggest that a larger portion of applied material stayed in the ground to work as intended instead of volatilize into the atmosphere. Due to the increased percentage of MITC retained in the ground, the possibility of reducing application rates for shank injection while maintaining product effectiveness should be considered.

In fall 2009 an experiment by this same lab was undertaken to look into this very possibility. Three rates of application are being compared, along with three different application methods (shank injection, standard chemigation, and drizzle boom modified chemigation) on a single field. This study is focused on efficacy of application methods and application rates. It is hoped this new research will give both growers and regulators more information when deciding which application method to use/encourage.

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Figure 2.1

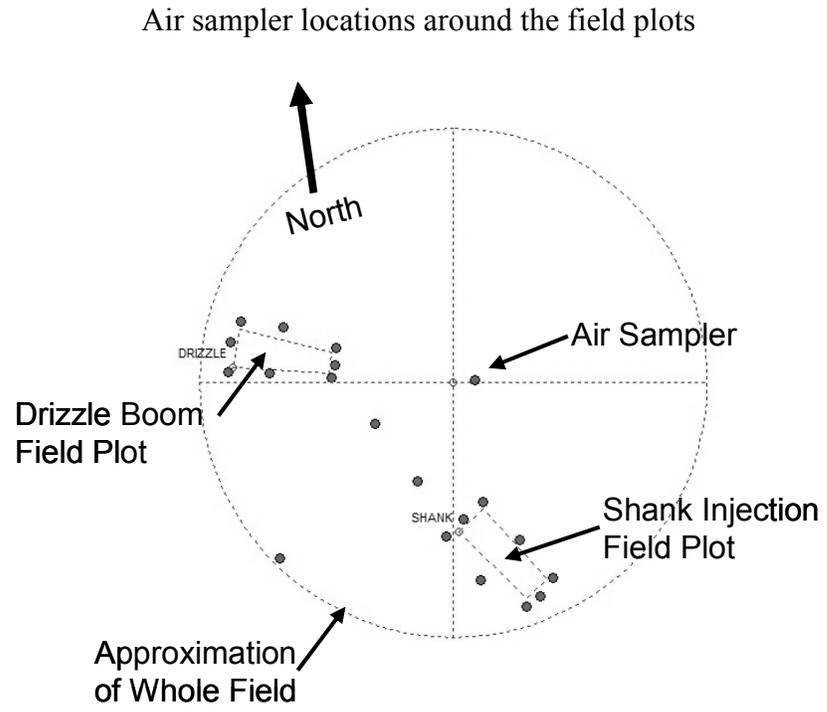
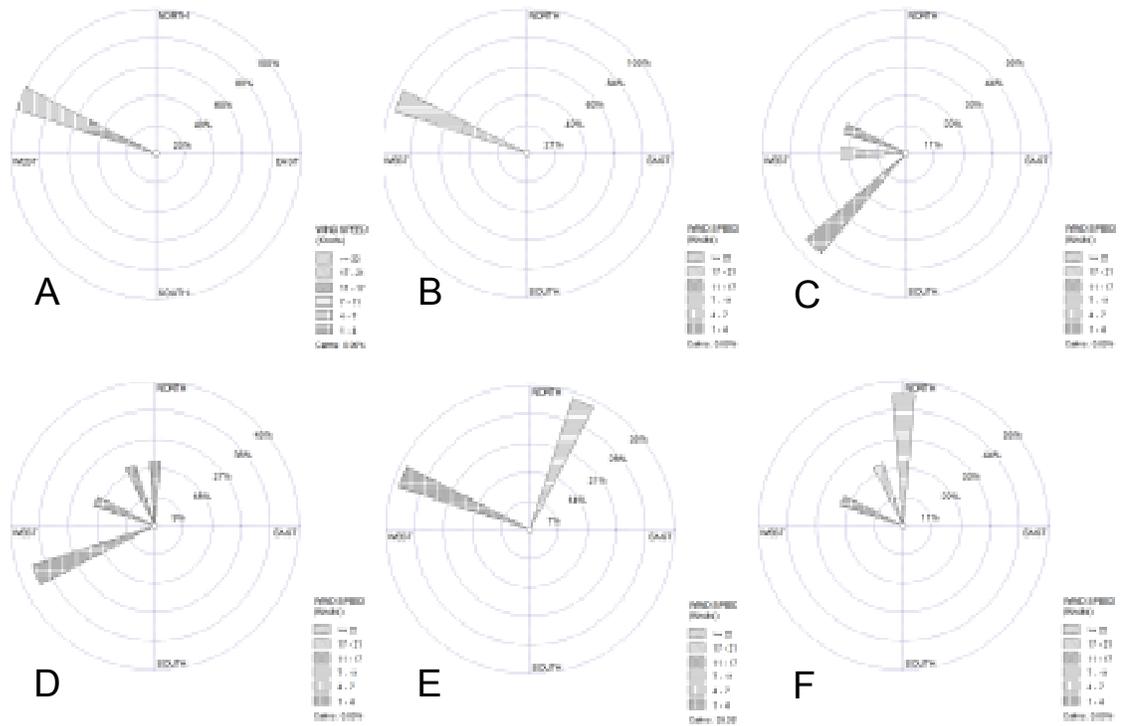


Figure 2.2. Wind rose plots for the first 6 sampling intervals



A) Application, B) 4 hours post application, C) 8 hours post application, D) 12 hours post application, E) 16 hours post application, F) 20 hours post application

Table 2.1 Whole Field Averaged MITC Concentrations

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

<sup>1</sup> Average value represent an average concentration of the eight samples,  
i.e. DB1-DB8, SH1-SH8

<sup>2</sup> MITC ppb = ( $\mu\text{g m}^{-3}$ ) x  $\frac{U8.21 \times 10^{-2} \text{ L-atm/mole-}^\circ\text{K} (298^\circ\text{K})}{(73.12 \text{ gram/mole}) (1 \text{ atm})}$

Figure 2.3. ISC-AERMOD View computer modeled concentrations using calculated flux values during application

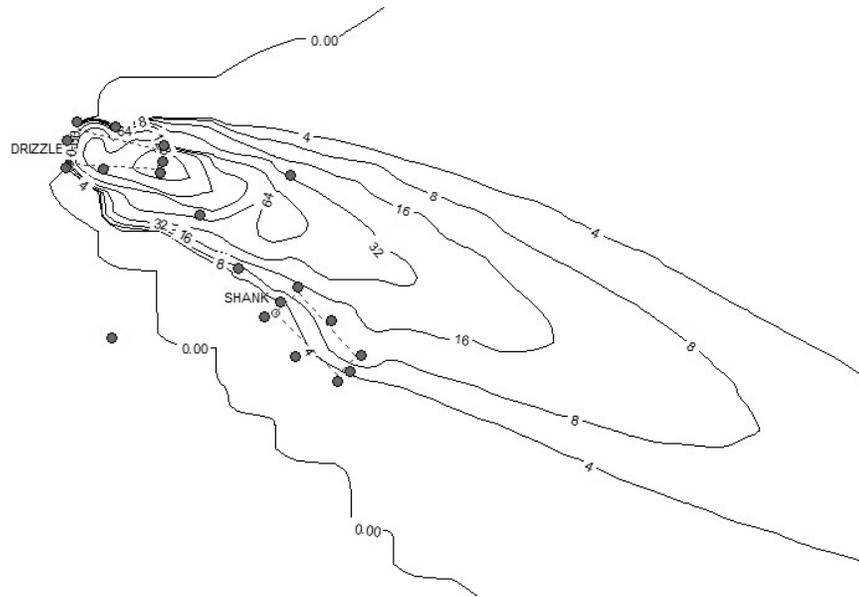


Figure 2.4. ISC-AERMOD View computer modeled concentrations using flux values for 16 hours post application interval

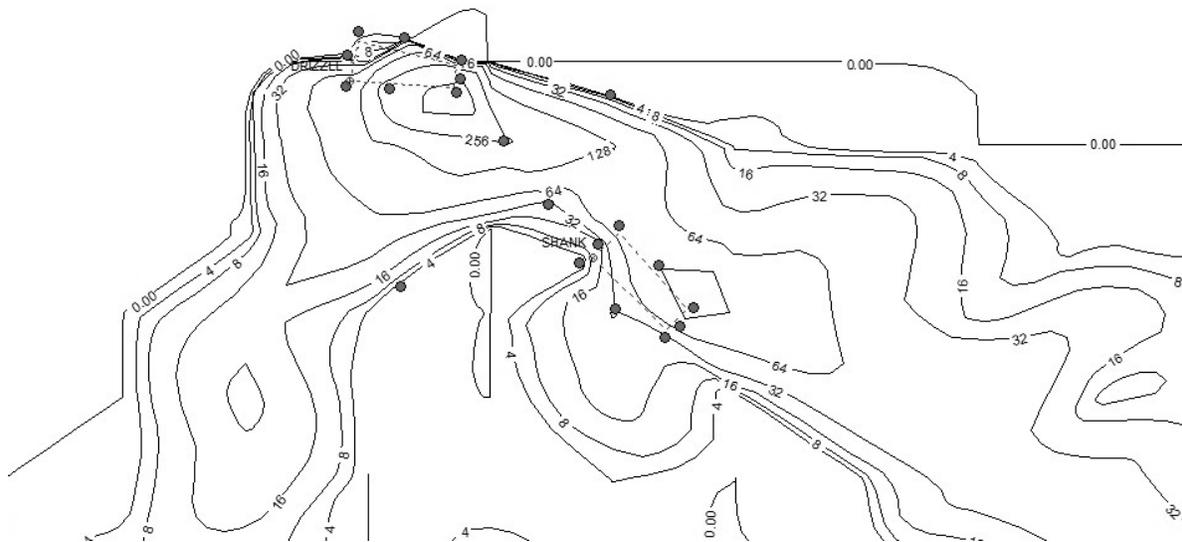
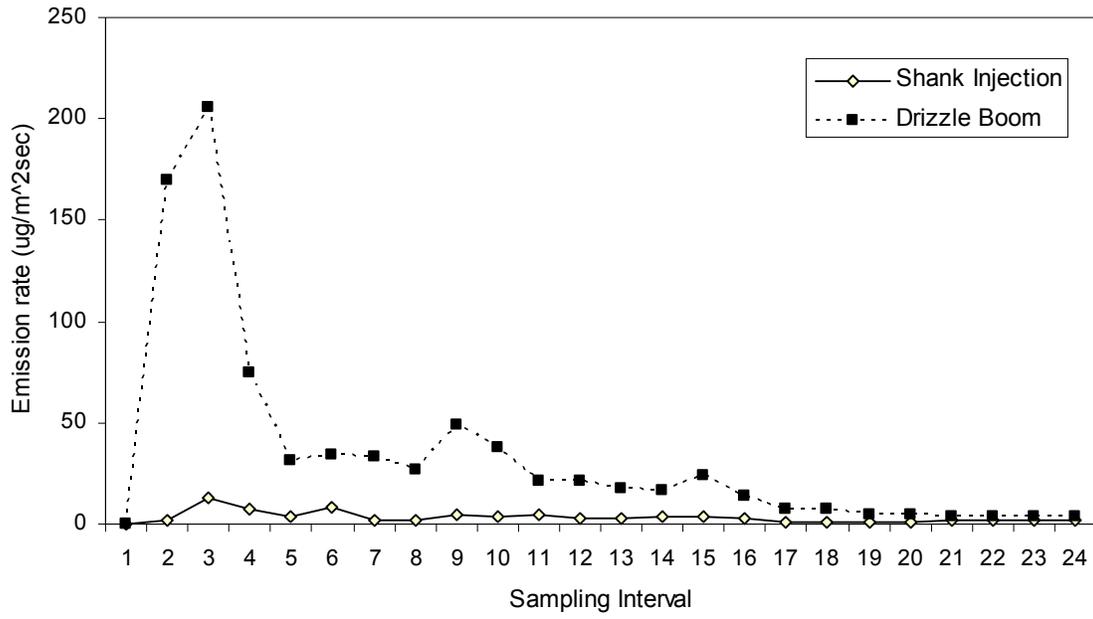


Figure 2.5 Comparisons of Flux Values for Shank Injection versus Drizzle Boom



**Attachment A**

Washington State University, Food and Environmental Quality Laboratory Project 0808

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

## **Section I. Executive Summary**

**Background:** In Washington State, potatoes are largely produced in the Columbia Basin and along the Snake River where water is available for irrigation. Center pivot sprinkler irrigation is used on about 90% of the potato acreage (PNW Potato PMSP, 2007). Counties in the Columbia Basin include: Adams, Benton, Franklin, Grant, Kittitas, Klickitat, Lincoln, Walla Walla, and Yakima (PNW Potato PMSP, 2007). This Basin accounted for 93% of potato acreage and 96% of production in Washington in 2005 on an estimated 150,000 acres of irrigation land (NASS, 2006). Potato is the major economic rotational crop. However, crop rotation is not only essential for nutrient loading but also for reducing the inoculum level of most endemic soil-borne disease organisms injurious to potatoes. In the Columbia Basin, rotations last 3 to 7 years and include grasses, wheat, corn, alfalfa, and miscellaneous vegetable crops.

Growers rely on the thiocarbamate fumigant metam sodium/potassium (trade names Vapam, Sectagon, Busan, and Metam CLR/KLR) hereto referred as metam, as a pre-plant soil fumigant to reduce the incidence of early die caused by *Verticillium* spp. Without the use of metam, this organism can significantly reduce quality and yield. Applications are typically performed by center pivot chemigation in the fall at a rate of ca. 170 lbs active ingredient per acre (i.e., 40 gallons of 40% metam per acre). Besides *Verticillium*, this product can be effective in controlling other soil-borne plant pathogenic organisms including certain soil surface nematode populations and various weeds. Reliance on this fumigant is largely a result of its effectiveness for soil-borne pathogen control and low cost of application. To apply by center pivot to a 120 acre circle, grower cost is ca. \$18,600 or \$155/acre. Keeping overall costs to a minimum is economically important in view of the fact that the grower must harvest ca. 27 tons per acre of quality potatoes to “break even” on investment (Hinman et al., 2007). While the majority of

metam use is prior to potato cropping, this material is also used during the production of other high value crops, also on a pre-plant basis, to control soil-borne plant pathogenic organisms.

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).

***Study Overview:*** This study was conducted from October 8<sup>th</sup> through the 13<sup>th</sup> to measure near-field MITC air emissions before, during, and through 4-days post application by two putative reduced application practices. Sectagon 42® (42% solution of metam sodium) was applied by

drizzle boom modified center pivot and shank injection at a rate of 71 gals/acre and 52 gal/acre for the drizzle boom and shank injection treatment plots, respectively. This rate of application is higher than the rate of 35-40 gal/acre used in Washington State for control of soil-borne pathogens in/on potatoes, but lower than the allowable maximum label rate of 75 gal/acre. Two field plots were laid out in one 122 acre circle (1.7 acres for drizzle boom and 1.8 acres for shank injection), 22 miles north of Pasco, Washington in Franklin County (see Figure 2). A more detail description of the test plot drizzle boom and shank applications can be found in Section II (Field Emission Summary) of this report. 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 (Figure 2). Figure 2 also shows the position of the CSAT3 3-D sonic anemometer employed to collect wind speed/direction data. 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.

Both field-scale fumigation events were conducted concurrently on October 8<sup>th</sup>. 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 (see Figure 3). 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. The collected charcoal samples from each monitoring site were

immediately stored on dry ice until they were brought on dry ice to the WSU-Food and Environmental Quality Laboratory (FEQL) where they were placed in a -80°C freezer.

The analytical method for quantifying MITC from activated charcoal was originally developed and validated in our facility for an earlier 2005 residential air monitoring study (WSU-FEQL, 2006). This method was adapted from a California Department of Pesticide Regulation method (“*Air Monitoring for Methyl isothiocyanate During a Sprinkler Application of Metam-Sodium*” Report EH 94-02, 1994) that relies on solvent extracting MITC from charcoal using a 80:20 proportion respectively of ethyl acetate to carbon disulfide followed by sonication and micro-filtration. Quantification was performed by gas chromatography with nitrogen phosphorus detection (GC-NPD). The analytical method for the measurement of MITC was found to be reliable and was validated in triplicate at 0.25 µg, 25 µg, and 300 µg total MITC to encompass the concentration levels detected in the air samples. The average MITC recovery from laboratory fortifications performed with each analytical sample set was  $95.5 \pm 9.3\%$  (n=95). Field fortification recoveries were  $92.9 \pm 4.2\%$  (n=3). Recovery from fortified trip blanks was  $95.4 \pm 3.5\%$  (n=5). The method limit of quantification (LOQ) was  $0.36 \mu\text{g}/\text{m}^3$  (0.12 ppb) and the limit of detection (LOD) was estimated to be  $0.07 \mu\text{g}/\text{m}^3$  (0.02 ppb) based on 1 L/min air flow for 8 hr sampling interval (~0.48 m<sup>3</sup> air sampled). A separate frozen storage stability study was not required since all samples were analyzed within 56 days of collection, well before the previously conducted 85-day storage stability evaluation for the 2005 air monitoring program (WSU-FEQL, 2006).

***Field-Measured MITC Emissions:*** Average 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 ( $417 \mu\text{g m}^{-3}$  (138 ppb)) with a maximum single observation near-field concentration during this time of  $963 \mu\text{g m}^{-3}$  (318 ppb). Maximum whole field-averaged MITC concentrations of  $78 \mu\text{g m}^{-3}$  (26 ppb) were observed 16-hours post application for the shank treated field with a maximum single observation near-field concentration of  $122 \mu\text{g m}^{-3}$  (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. Detailed MITC concentration results from each air monitoring cartridge for drizzle boom modified chemigation and shank injection are respectively provided in Tables 4 and 5 and respectively illustrated in Figures 7 and 8.

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-shanking, the maximum observed single air monitor concentration of 40 ppb ( $122 \mu\text{g m}^{-3}$ ) was observed (see Table 5 and Figure 8). Measured MITC concentrations from air monitoring receptor locations positioned equidistantly between the two test plots (W and Y locations, Figure 3) indicate downwind emissions towards the shank plot over this interval period (also see Table

6 and Figure 9). Although all attempts were made to position test plots to minimize cross-contamination, it is reasonable to state that directional MITC drizzle boom source emissions contributed to the measured shank emission estimates, especially during the first 20 hours of this field demonstration, which conservatively represents the shank injection emission estimates

***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 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) Emissions Assessment Method criteria (see Appendix F) 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  $> 95^{\text{th}}$  percent confidence level) and the intercept term was not significant (signifying the  $95^{\text{th}}$  percent confidence level included the origin). If the slope was not significant or the intercept term was significant, then the least squares regression method had to be applied forcing the slope through 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. Periodically, other conservative default factors were employed for estimation when the modeled/measured emissions could not be calculated. Following the technical procedures outline by Cal DPR's emission estimation process in Appendix F, the estimated total cumulative MITC loss by drizzle boom was calculated to be 47% compared to 12.6% by soil incorporated shank injection (total cumulative loss here assumes a 1:1 molar stoichiometry, complete conversion of metam sodium to MITC, and loss is by surface emission after application). Figure 1 illustrates the relative emission rates of drizzle boom to shank over the continuous 4-day application/post application time frame.

Drizzle Boom: It was found that drizzle boom test plot measured and modeled emission data were well ordered and usually were well correlated allowing emission rate estimation by slope. Notable exceptions were for one interval (Period 4, see Table 1) where a pronounced and strong wind shift occurred before the end of this monitoring period, which resulted in poor measured to normalized modeled concentration correlation (see Appendix F). For this period, the use of hourly-averaged wind direction that could not account for a sudden directional shift could explain the lack of association among receptor measured and modeled emission values. Due to poor linear correlation, the generally more conservative mean measured/mean model approach was also applied for the last four periods when low measured MITC receptor concentrations likely resulted in the observed greater measured to modeled variation.

Soil Incorporated Shank Injection: The wind direction during the first five 4-hr air monitoring periods predominated from the Northwest from the higher upwind emission drizzle boom plot

location towards the lower emission downwind shank test plot (see Figures 2 and 3). This downwind MITC contribution influenced the reliability of using a linear slope for field measured/modeled emission flux estimation at the shank plot. As a result, shank flux estimates were generated by the more conservative mean measured/mean flux estimation Cal DPR approach at application and up to the first five post-application periods. The occurrence of low MITC emissions at two off-field receptor locations (W and Y) located approximately equidistant between the two test plots (see Table 6 and Figure 9) further corroborated that concentrations from the drizzle boom test plot enhanced MITC concentrations at the more northwesterly shank receptor locations. From the above it is reasonable to infer that MITC source contributions from the higher emission drizzle boom plot influenced the capability of relying on linear regression for estimating flux from field measured versus modeled emissions over the first five 4-hour receptor collection periods.

It is important to note that measured MITC emissions from the shank plot when compared to the drizzle boom plot were appreciably lower during and through the 4-day post application time frame (see Figures 1, 7 and 8). It is reasonable to conclude that downwind drizzle boom source contributions highly influenced shank assessment methods that rely on linear goodness of fit. To more accurately calculate emission rates from plots downwind from other treated plots, Cal DPR (2006) first generated emission rates for the upwind plots and utilizing the back calculated emission rate values, estimated MITC concentrations for downwind receptors after background subtraction. The reported emission rates in Appendix F were performed without employing background subtraction because a procedure such as employed by Cal DPR (2006) was not found to be appropriate for this data set. . When defaulting to a more conservative approach for periods where measured field concentrations do not correspond well to modeled predictions, it is

reasonable to anticipate over-estimation of actual field emission rates. This especially would be expected under circumstances where higher near-field source contributions can mask actual field emissions from reduced-emission application techniques such as shank.

In ending, this field-scale 2008 reduced-emission application information provides regionally specific emission flux data typical of the cooler fall climatic conditions when PNW fumigations are occurring. Field emission estimates and on-site field CSAT meteorological data for generating flux and cumulative MITC loss can be downloaded from <http://feql.wsu.edu/data/>.

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**Table 1**  
**Whole Field Averaged MITC Concentrations**

Approximate Hours post fumigation	Assigned Period	Drizzle Boom average <sup>1</sup> MITC air concentration		Shank Injection average <sup>1</sup> MITC air concentration	
		( $\mu\text{g}/\text{m}^3$ )	(ppb) <sup>2</sup>	( $\mu\text{g}/\text{m}^3$ )	(ppb) <sup>2</sup>
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

<sup>1</sup> Average value represent an average concentration of the eight samples, i.e. DB1-DB8, SH1-SH8

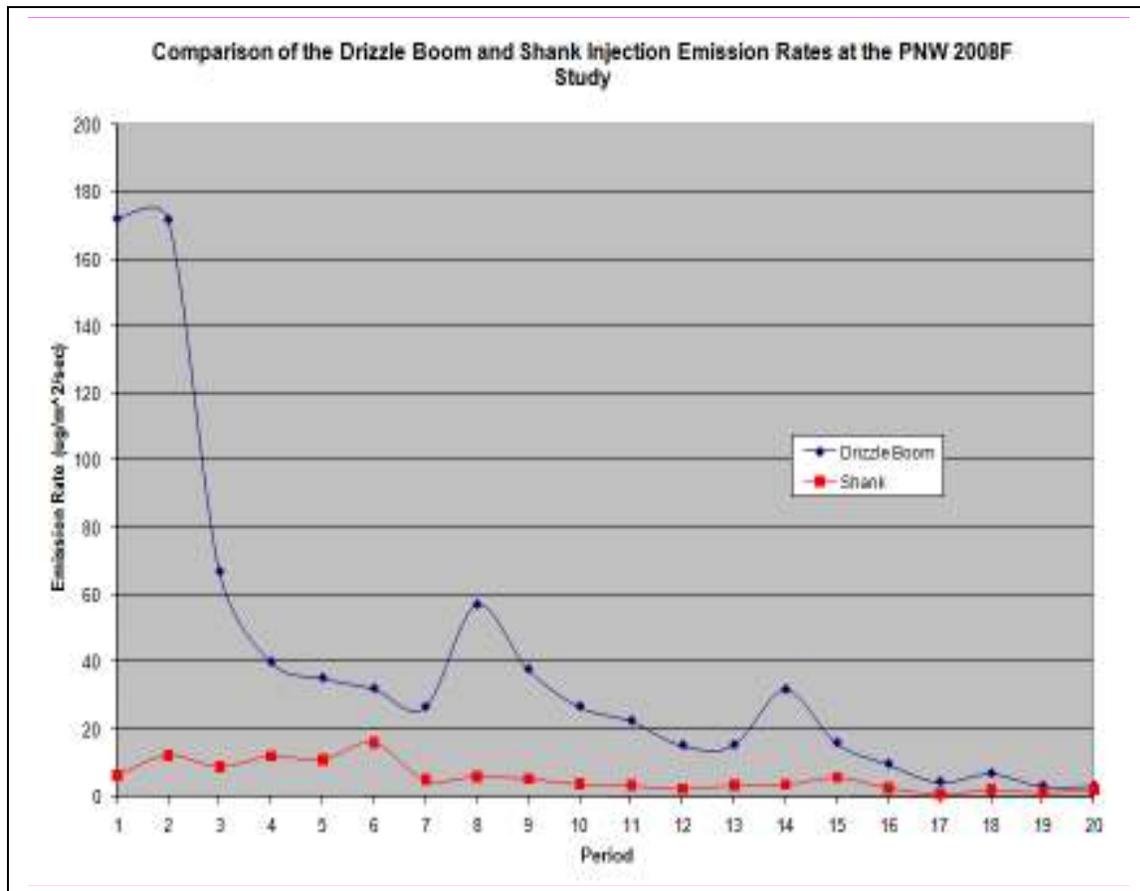
$$^2\text{MITC ppb} = (\mu\text{g m}^{-3}) \times \frac{U(8.21 \times 10^{-2} \text{ L-atm/mole-}^\circ\text{K})(298^\circ\text{K})}{(73.12 \text{ gram/mole})(1 \text{ atm})}$$

**Table 2**

**Maximum Measured MITC air concentrations**

Air sampler identification	Maximum air concentration detected ( $\mu\text{g}/\text{m}^3$ )
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)

**Figure 1: Comparison of Drizzle Boom and Shank Injection Emission Rates: October 8<sup>th</sup> through the 13<sup>th</sup> 2008, Franklin County, WA \***



\* See Table 1 for interval sampling hours corresponding to each period

## Section II. Field Emission Study

### A. Test Plot Locations

#### *Summary:*

This field study was designed for two separate metam sodium applications to be conducted concurrently on separate test plots within a single center pivot field typical of the region. The field site was located near Eltopia, Franklin County, WA. The field site was a 122 acre, eight tower center pivot circle rotating out of sweet corn into potato. The field was disk plowed and watered prior to fumigant application. This study was conducted in early-October during a time when fumigation occurs throughout the region.

Two separate ca. 2 acre field plots were selected for shank injection and drizzle boom chemigation (Figure 2). 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. Three days prior to application the air samplers and weather station were setup, and exact locations were recorded via GPS (Table 3a, b, c). TKI provided Sectagon 42 for drizzle boom modified center pivot chemigation and shank applications.

#### Test Substance:

Trade Name:	Sectagon 42 <sup>®</sup>
EPA Reg. No:	61842-6
Active Ingredient:	Dithiocarbamate salt solution
Common Name:	Sodium Methylthiocarbamate,

*Drizzle boom modified center pivot chemigation:* Sectagon 42<sup>®</sup> was applied to a ca. 1.7 acre plot section (see Figure 2). Center pivot towers 1-3 and 8 were capped off during this trial and towers 4 through 6 were modified for low drift drizzle boom attachment. This horizontal boom constructed of PVC piping was attached to existing sprinkler heads allowing application 2-3 feet from the soil surface. Sectagon 42 was applied with 1 inch of water to set the product

within the soil. The start and stop times for this application were respectively 11:35 am and 1:30 pm, October 9, 2008. A total of 120 gallons of Sectagon 42 was applied over this 1 hour 55 minute application period, which represents a 71 gal/acre application.

Soil-incorporated shank injection: On October 9<sup>th</sup>, 2008 starting at 12:10 pm, Sectagon 42<sup>®</sup> was applied at a rate of 52 gal/acre to a 1.8 acre field plot by shank injection at a ca. depth of 9 inches followed by soil compaction. The application took place during a 40 min time frame using a total of 93 gallons of product. This test plot was “double disk plowed” before application to allow uniform penetration of the blades to the required depth.

Receptor siting: The eight receptors at each field plot were positioned ca. equidistantly and ca. 15 meters from the treated edge (Figure 3). Four additional ambient air receptors were positioned between the two treatment plots (Figure 3), one near the center of the center pivot circle (X), one near the southwest circle field corner (Z) and two near equidistant between the drizzle boom (Y) and shank injection plot (W). These additional receptor sites were included to evaluate potential contribution of off-target MITC emissions over the experimental time frame. The location of each air monitoring position was recorded using a Garmin Trex Legend GPS (Table 3a, b and c). Receptors were positioned from #1 to #8 in a clock-wise manner starting at the southwest corner of each test field plot. MITC in ambient air was monitored pre-application, during fumigation and at either 4 or 8 hour periods through 4 days post-application. A mast was constructed for each receptor location (Figure 4). Each receptor location consisted of an SKC personal air sampling unit (SKC Model PCXR4) placed at the base of a sampling mast in a protective case, with a vertical ca. 1.5-meter height crossbar. Tubing was used to connect to the 600 mg charcoal-filled cartridges (SKC # 226-09) located at the end of the crossbar (Figure 4). Each air sampler pump was powered by a heavy duty

marine battery connected via a SKC battery eliminator (SKC #223-325). Prior to the start of sampling, the deep cycle battery was found to be able to run the pump for over 7 days consecutively at 1 L/min. The two co-located samplers per plot location relied on the same battery. Air flows were measured and recorded at the start and end of collections.

Table 3a

GPS Locations of Drizzle Boom Site and Receptor Locations

<b>NW Corner</b>	N46 29.522 W119 07.857
<b>NE Corner</b>	N46 29.505 W119 07.745
<b>SE Corner</b>	N46 29.487 W119 07.747
<b>SW Corner</b>	N46 29.490 W119 07.865
<b>DB1</b>	N46 29.488 W119 07.865
<b>DB2</b>	N46 29.511 W119 07.869
<b>DB3-L,-R</b>	N46 29.529 W119 07.857
<b>DB4</b>	N46 29.525 W119 07.805
<b>DB5</b>	N46 29.509 W119 07.739
<b>DB6</b>	N46 29.495 W119 07.742
<b>DB7-L,-R</b>	N46 29.484 W119 07.758
<b>DB8</b>	N46 29.489 W119 07.821

Table 3b

GPS Locations of Shank Injection Site and Receptor Locations

<b>NW Corner</b>	N46 29.357 W119 07.583
<b>NE Corner</b>	N46 29.377 W119 07.555
<b>SE Corner</b>	N46 29.319 W119 07.474
<b>SW Corner</b>	N46 29.302 W119 07.498
<b>SH1</b>	N46 29.295 W119 07.499
<b>SH2</b>	N46 29.317 W119 07.538
<b>SH3</b>	N46 29.353 W119 07.599
<b>SH4-L,-R</b>	N46 29.368 W119 07.578
<b>SH5</b>	N46 29.382 W119 07.555
<b>SH6</b>	N46 29.352 W119 07.509
<b>SH7</b>	N46 29.320 W119 07.467
<b>SH8-L,-R</b>	N46 29.304 W119 07.486

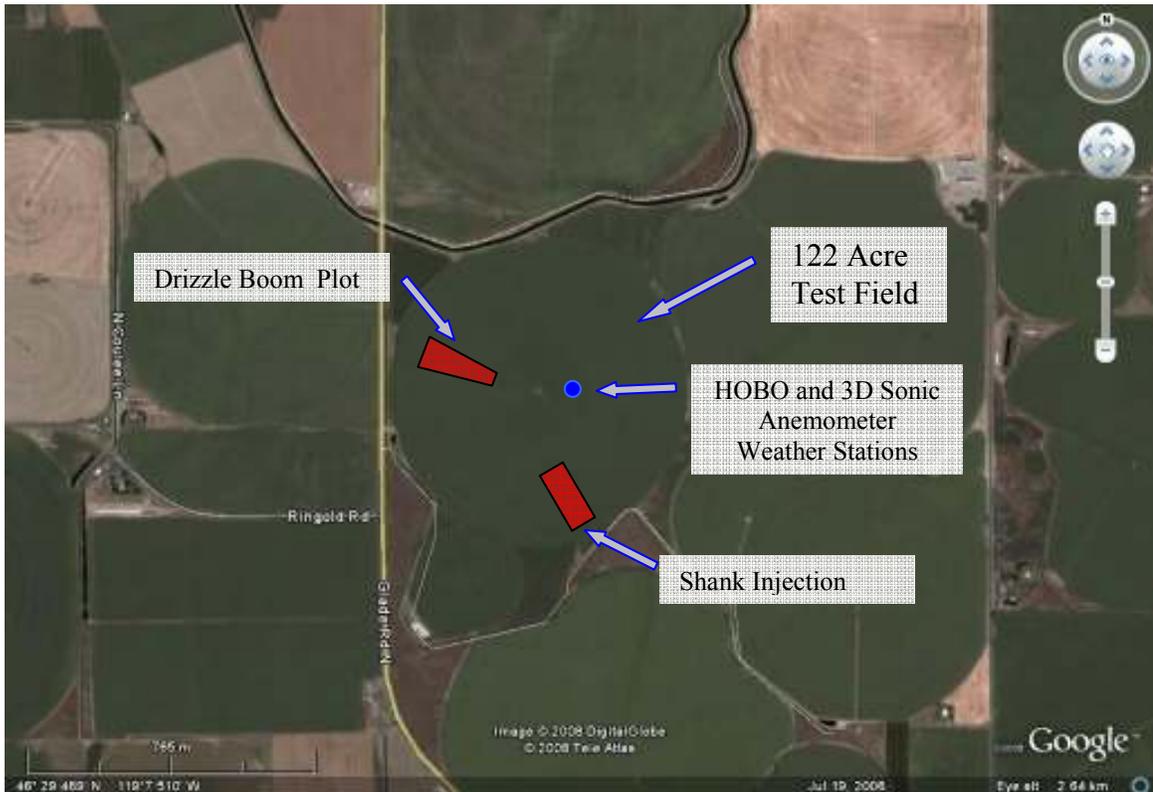
Table 3c

Emission Monitors and Weather Station

<b>Hobo Weather Station</b>	N46 29.483 W119 07.573
<b>3-D Sonic Anemometer</b>	N46 29.482 W119 07.572
<b>Air Monitor W</b>	N46 29.398 W119 07.636
<b>Air Monitor X</b>	N46 29.485 W119 07.569
<b>Air Monitor Y</b>	N46 29.446 W119 07.689
<b>Air Monitor Z</b>	N46 29.330 W119 07.802

Figure 2

Location of Field  
Approximately 22 miles north of Pasco, South Franklin County, Washington State  
Intersection of Ringold Rd and N. Glade Rd. \*



\*Google Earth 2008

**Figure 3**  
Receptor locations surrounding test field plots

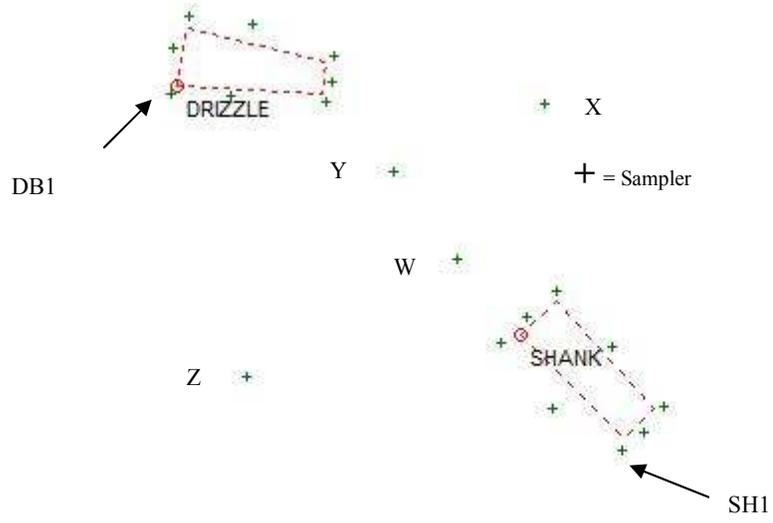
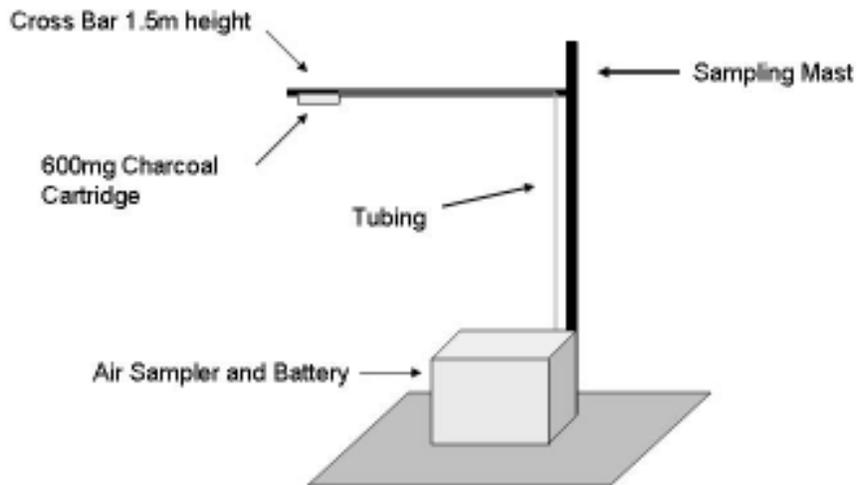


Figure 4

**Schematic of receptor mast**



## B. MITC Receptor Locations

MITC in air was trapped on activated charcoal before, during, and through 4-days after center pivot chemigation and shank injection. The air sampling receptors at both plot locations were operated continuously. Four-hour monitoring was conducted pre-application and through the first two days of post-application air monitoring. Eight-hour monitoring was continuously performed over the last two days of the emission study. A four-hour pre-application ambient air sampling period was conducted at each plot location prior to field treatments. Drizzle boom chemigation began the morning of Oct. 9 (11:35 am), shank injection was started 40 min later (12:10 pm), to time the end of the applications concurrently. Shank injection application took place over a ca. 45 minute period while the drizzle boom chemigation took ca. 2 hours to complete.

At the start and end of receptor collections, flow measurements were recorded by rotometer. An average flow rate for the two measured flows was used to calculate total period air flow (Appendix B, Sample Inventory; Tables 10, 11, and 12). Typically, beginning/ending flow rate measurements through the activated charcoal cartridge were uniform at ca. 1 L/min air (i.e., ca. 0.24 m<sup>3</sup> total air sampled in a 4-hour time period or ca. 0.48 m<sup>3</sup> in 8 hours).

After each sample interval the activated charcoal cartridges were collected and immediately placed in a cooler with dry ice. Samples were intermittently transported on dry ice (with quality control samples) to the WSU-Food and Environmental Quality Laboratory (FEQL) where they were stored at -80 °C until analysis. A separate frozen storage stability study was not conducted since all samples were analyzed within 56 days of collection, well before the previously conducted 85-day storage stability evaluation conducted for the 2005 air monitoring program (WSU-FEQL, 2006).

Sample Coding: The samples acquired from the field were given a unique sample code. This code was constructed so that each individual sample at each site location was traceable. The coding designations were as follows:

<b>Field &amp; Air Sample Designation</b>	<b>Air sampler number</b>	<b>Time Interval Code</b>	<b>Collocation (Right/Left)</b>	<b>Date of sample start</b>
DB (Drizzle Boom)	1-8	A, B,C,D,E,F etc.	R/L (DB3 and 7 only)	mmddyy
SH (shank injection)	1-8	A, B,C,D,E,F etc.	R/L (SH4 and 8 only)	mmddyy
W,X,Y,Z	NA	A, B,C,D,E,F etc.	NA	mmddyy

Appendix B provides a complete list of sample inventory and sampling duration. Tables 10 and 11 of Appendix B list the drizzle boom and shank injection samples, respectively. Table 12 lists the sample inventory for receptor locations between the two treatment plot locations.

### C. Quality Control Samples

#### i. Trip Blanks

Every sample shipment included a trip blank cartridge which accompanied the shipment set. The trip blank was an unfortified cartridge prepared and transported to the field and back to the lab with the field samples. Trip blank samples are noted with a “TB” designation. Trip blank and fortified trip blank samples were kept together with the collected field receptor samples through chemical analysis.

#### ii. Field Fortifications

During the post-fumigation air monitoring period, activated charcoal cartridges were fortified with a known amount of MITC at the FEQL facility and attached to an air sample pump at air flow rates similar to what was used for the field samples. Field fortifications (together with their associated control blank cartridges) were performed to verify quantitative retention of the MITC on the activated charcoal over the longest period of air sampling. The 600 milligram cartridge

field fortification was run for both four and eight hours outside on the WSU Richland campus. The average MITC recovery from field fortifications was  $94 \pm 2.7\%$  (n=3) (see Table 9). The eight-hour control contained quantitative (but low) levels of MITC. Background MITC concentrations were subtracted before calculating percent recovery.

### iii. Fortified Trip Samples

Additionally, spiked trip samples were used to ensure integrity from the field through laboratory frozen storage, to chemical analysis. Fortified trip blanks are noted with a “SB” designation. Cartridges were spiked with 100 µg MITC and transported to the field during sample intervals, and were returned with the field samples to FEQL to simulate handling of the air monitoring samples. The average recovery from the 600 mg fortified trip blanks was  $95 \pm 3.5\%$  (n=5) (see Table 9).

### D. Meteorological Data

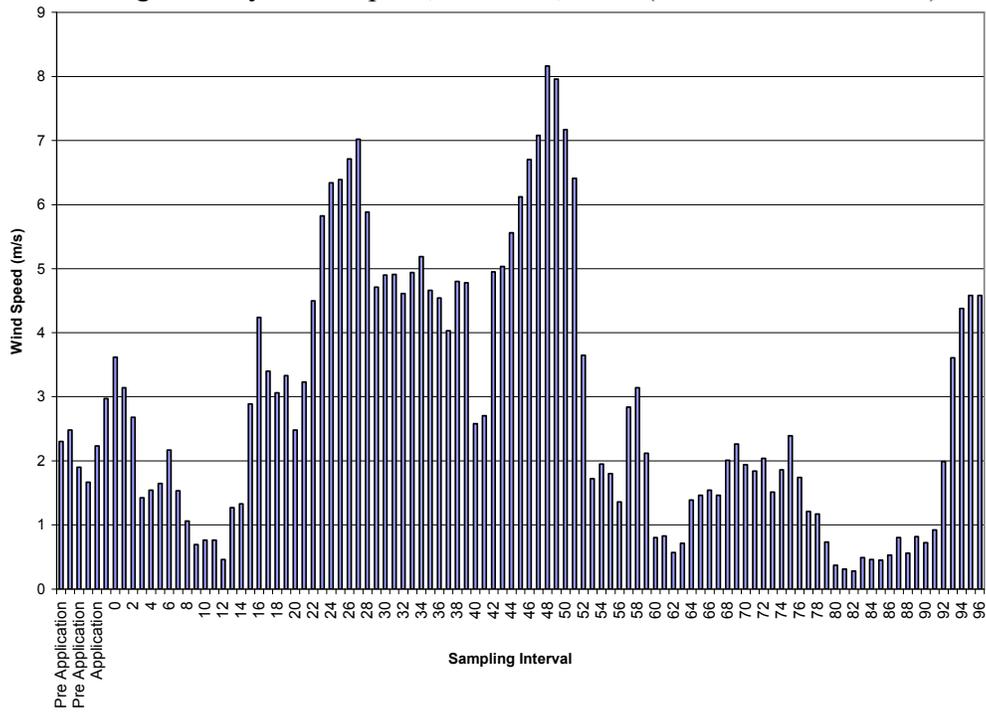
Wind speed/direction (Onset Computer Corporation<sup>®</sup> part #S-WCA-M003), air/soil temperature (S-TMB-M006), soil moisture (S-SMA-M005) and rainfall (S-RGA-M006) data were collected throughout the pre-application, fumigation and air sampling time period starting October 7, 2008 with an Onset HOBO Weather Station data logger<sup>®</sup> (H21-001). Wind speed and direction were recorded at a 2 meter height (*these wind data were not used in emission rate calculations*). Soil temperature and soil moisture levels were recorded at 6” depth by the HOBO system. This Onsite weather station was located in the center of the field north of the shank injection plot and east of the drizzle boom field (see Figure 2). A CSAT3 3-D sonic anemometer was employed to

collect wind speed/directional data used in MITC emission rate assessments and also positioned in close proximity to the HOBO system (see Figure 2). The CSAT unit was maintained by Sullivan Environmental Consulting Inc. Average air temperature over the sampling interval was approximately 7.7°C (45.9 °F) with a high of 18.9°C (66 °F) and a low below freezing (-1.5°C or 29.3°F ). Average 6” depth soil temperature during the trial was 10.2 °C (50.4 °F), with a high of 15.7 °C (60.3°F) and a low of 6.2 °C (43.2°F ). The measured soil moisture level (at 6” depth) dropped from 1.41 m<sup>3</sup>/m<sup>3</sup> at the beginning to 0.094 m<sup>3</sup>/m<sup>3</sup> by the end of the sampling period. No measurable rainfall was recorded. Complete averaged hourly weather data for the above listed parameters (excluding CSAT data) is provided in Appendix C. Figure 5 is a HOBO Weather Station plot of wind speed for the duration of the fumigations. Figure 6 provides a summary profile of both ambient air and soil temperatures over the experimental period. The complete CSAT wind speed data set used in calculating MITC emission rates can be found at <http://feql.wsu.edu/data/>.

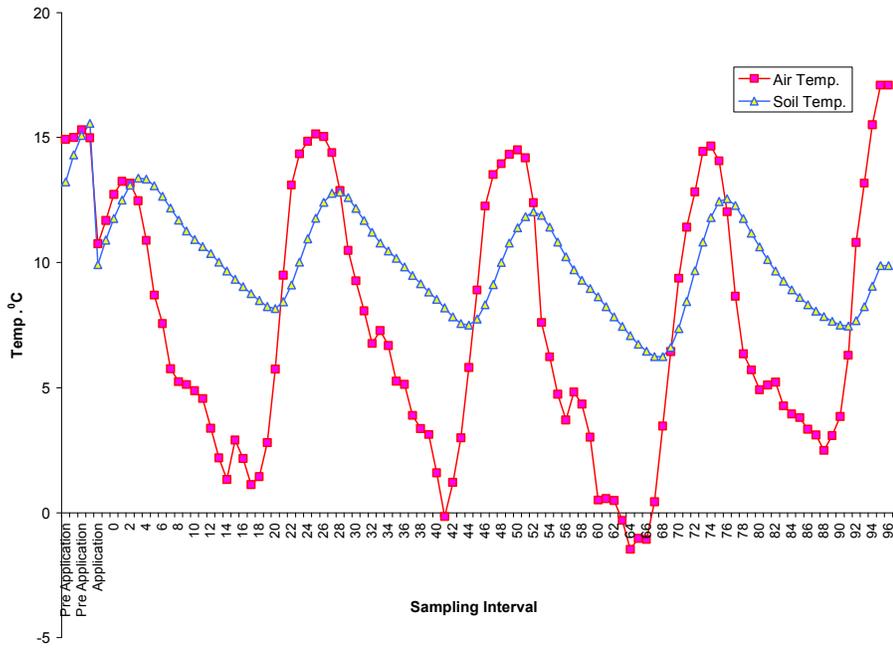
#### E. Encountered Field Related Problems

Periodically pump failures were encountered, more so at the W receptor location. Out of 546 individual receptor evaluations, 5 receptor failures were recorded (i.e., < 1% failure rate).

**Figure 5**  
Average Hourly Wind Speed, Oct 8-13, 2008 (HOBO Weather Data)



**Figure 6**  
Average Hourly Air and Soil Temperature Oct 8-13, 2008 (HOBO Weather Data)



### Section III. Analytical Summary

#### A. Working Analytical Method

The analytical method used for assessing MITC from air was identical to the method we followed in 2007 (LePage and Hebert; 2008). This analytical method is based on a California Department of Pesticide Regulations (Cal DPR) solvent extraction method using 20% carbon disulfide, 80% ethyl acetate (“*Air Monitoring for Methyl isothiocyanate During a Sprinkler Application of Metam-Sodium*” Report EH 94-02, 1994) for determining methyl isothiocyanate (MITC) from activated charcoal sampling cartridges. Samples extracts were then analyzed by gas chromatography with nitrogen phosphorus detection (GC/NPD). Additionally, each analytical set was run with concurrent quality control blank and fortified charcoal matrix samples. The working method for this study is provided as Appendix D.

#### B. Quantitation

##### i. Standard Preparation

Standards were prepared to bracket the range of MITC concentrations expected in the charcoal samples. The following test substances, standards, and standard dilutions were employed in this study:

##### Test substance

<b>Compound</b>	<b>Substance No.</b>	<b>Purity</b>	<b>Source</b>
Methyl isothiocyanate	1356	99.5%	Chem Service

##### Stock Solution

<b>Compound</b>	<b>Substance No.</b>	<b>Conc.</b>	<b>Solvent</b>
Methyl isothiocyanate	13561	10 mg/mL	methanol

##### Dilutions of Stock Solution

<b>Compound</b>	<b>Substance No.</b>	<b>Conc.</b>	<b>Solvent</b>
Methyl isothiocyanate	135614	20 µg/mL	20% CS <sub>2</sub> /ethyl acetate

Methyl isothiocyanate	135615	15 µg/mL	20% CS <sub>2</sub> /ethyl acetate
Methyl isothiocyanate	135616	10 µg/mL	20% CS <sub>2</sub> /ethyl acetate
Methyl isothiocyanate	135617	5 µg/mL	20% CS <sub>2</sub> /ethyl acetate
Methyl isothiocyanate	135618	2 µg/mL	20% CS <sub>2</sub> /ethyl acetate
Methyl isothiocyanate	135619	1 µg/mL	20% CS <sub>2</sub> /ethyl acetate
Methyl isothiocyanate	13561-10	0.5 µg/mL	20% CS <sub>2</sub> /ethyl acetate
Methyl isothiocyanate	13561-11	0.1 µg/mL	20% CS <sub>2</sub> /ethyl acetate
Methyl isothiocyanate	13561-12	0.05 µg/mL	20% CS <sub>2</sub> /ethyl acetate
Methyl isothiocyanate	13561-13	0.025 µg/mL	20% CS <sub>2</sub> /ethyl acetate

#### Fortification Solutions

<b>Compound</b>	<b>Substance No.</b>	<b>Conc.</b>	<b>Solvent</b>
Methyl isothiocyanate	135613	10 µg/mL	methanol
Methyl isothiocyanate	135612	100 µg/mL	methanol
Methyl isothiocyanate	135611	1 mg/mL	methanol
Methyl isothiocyanate	13561	10 mg/mL	methanol

All standard solutions were stored at approximately –20 °C (I.D. Prancer). The expiration date for the reference substance was 04/2009. Dilutions are recorded in the FEQL analytical laboratory standards logbook. The expiration date of these MITC standards was 4/2009.

#### ii. Instrumentation

A Varian Star 3400CX gas chromatograph with nitrogen-phosphorus specific detection (NPD) and an 8200CX autosampler was used for residue detection and quantitation (instrument ID: Curly). Integration of chromatographic data was performed using Varian Star Chromatography Workstation software.

Column: Alltech EC-WAX, 15m x 0.53mm, 1.20 µm film thickness

Carrier gas: Ultrapure helium,  
column flow rate ca 3.5 mL/min at 55 °C.

Temperatures: Detector: 260 °C  
Injector port: 55 °C to 225°C (rate: 225°C/min), hold 5 min.

Oven program: Initial: 55°C, hold for 0.09min.  
Ramp 10°C/min to 90°C, hold for 5 min.

MITC Retention time: 6.3 min (+/-0.1 min)  
Detector: NPD bead current 3.1-3.2 A  
Injection volume: 2 µL

iii. Calculations

The quantification of MITC concentrations in the charcoal air sample cartridges were performed by electronic peak area measurement and comparison to the linear regression from a minimum of four external standards in the concentration range of the matrix-sample concentrations. To assure high quality during GC operation, all samples were bracketed with external calibration standards during the analytical set. Linearity and calibration standards were then used to construct the calibration curve using a spreadsheet program (Microsoft Excel<sup>®</sup>). The MITC air concentration is calculated according to equations 1 and 2.

Eq 1: Total conc. (µg) = (x µg/mL detected concentration) (Final volume of extract)

For example, sample set 0808-26, dated 11/13/2008 included the preparation of air sample SH6-H-101008 (shank injection, sampler #6, time period H, air sample cartridge, date 101008). The sample was processed for analysis to a final volume of 5 mL. The MITC linear regression line of best fit calculated from calibration standards ( $R^2 = 0.999$ ) of this set was:

Y (peak area)= m(slope) X(detected concentration in ug/mL) + b(intercept)

$$Y = 35674.6 X + 35.5$$

The MITC-peak area count for this sample was 9630. Therefore, the concentration (in µg/mL) was:

$$9630 = 35674.6 X + 35.5$$

$$X = \frac{(9630 - 35.5)}{35674.6} = 0.269 \mu\text{g/mL}$$

The total concentration is then calculated according to Eq. 1:

$$0.269 \mu\text{g/mL} \times 5 \text{ mL} = 1.34 \mu\text{g MITC}$$

To determine air concentration, the total MITC concentration was divided by the volume of air sampled, Eq. 2. The volume of air was found by multiplying the average flow rate (L/min) by the total minutes of sampling, and converting from liters to m<sup>3</sup>.

$$\text{Eq.2: MITC air concentration } (\mu\text{g/m}^3) = X \mu\text{g MITC} / \text{total air sampled (m}^3)$$

From the example above, the air sampler operated at an average flow rate of 0.95 L/min from 7:16 am to 10:59 am or 223 minutes.

$$(0.95 \text{ L/min})(223 \text{ min}) = 212 \text{ L}$$

$$(212 \text{ L})(1 \text{ m}^3/1000 \text{ L conversion factor}) = 0.21 \text{ m}^3 \text{ air sampled}$$

Therefore by equation 2, MITC air concentration

$$X (\mu\text{g/m}^3) = 1.34 \mu\text{g MITC} / 0.21 \text{ m}^3 = 6.35 \mu\text{g/m}^3 (2.09 \text{ ppb}) \text{ MITC}$$

To assess overall analysis precision and percent recovery, control cartridges were fortified with a known amount of MITC prior to extraction. For each analytical set, percent recovery for the fortified sample was calculated using peak areas according to equation 3.

$$\text{Eq.3: \% Recovery} = \frac{(\text{Fortified Peak} - \text{Control Peak})\text{Calculated Conc.} \times 100}{\text{Fortification Amount}}$$

For example, a control cartridge included in set 0808-21 (0808FS57), was fortified with 25 µg of MITC. The sample extract was prepared to a final volume of 5 mL for MITC determination. The MITC peak area count for this fortified sample was 180344. The peak area count for its corresponding control at the same dilution was 0 area counts. The fortified sample concentration calculated from the linear regression for this set is 4.702 µg /mL MITC.

The total concentration is then calculated according to Eq. 1:

$$4.702 \text{ µg /mL} \times 5 \text{ mL} = 23.51 \text{ µg MITC}$$

From Eq. 3, the percent recovery for this fortified sample was:

$$\text{Percent Recovery} = \frac{23.51 \text{ µg}}{25 \text{ µg}} \times 100 = 94.0\%$$

### C. Method Validation and Analytical Limits

Prior to the analysis of any samples, the working method was validated by fortifying and recovering MITC from 600 mg cartridges, which are identical to the cartridges used in this field study. The method was considered validated if recovery of MITC was within the range of 70%-120% with a standard deviation of <20%. The method was validated in triplicate at 0.25 µg MITC to establish a limit of quantitation (LOQ). The method LOQ for air samples was established at 70% of the lower limit of method validation (0.25 µg total MITC) or approximately 0.36 µg/m<sup>3</sup> based on 1 L/min air flow for 8 hr sampling interval (~0.48 m<sup>3</sup> air sampled). The limit of detection (LOD) was estimated to be approximately one-fifth of this value or 0.07 µg/m<sup>3</sup> based on 1 L/min air flow for 8 hr sampling interval (~0.48 m<sup>3</sup> air sampled). The method was also validated at 25 µg, and 300 µg MITC to encompass anticipated concentration levels. Table 7 provides the method validation results.

In addition to method validation, fortified matrix samples were extracted concurrently with study samples. The sample set was considered acceptable if the fortified recovery was within the range of 70%-120%. Table 8 includes results from the fortified samples extracted during sample analysis.

#### D. Storage Stability Study

A storage stability evaluation for MITC on charcoal-filled glass cartridges was completed by the FEQL in 2005 (MITC Community Air Assessment. Analytical Summary Report, FEQL-NG-0605). MITC was found to be stable on the cartridges stored at -80°C for a period of 85 days. For this 2008 field fumigation air monitoring project, no receptor charcoal cartridges were stored at  
-80 °C for more than 56 days.

#### E. Interferences

There were no interferences in the chromatographic window for MITC.

#### F. Confirmatory Techniques

Analytical standards were used to confirm the presence of MITC by retention time.

#### G. Time Required For Analysis

The time required for an experienced person to work up a set of samples (10 samples plus 1 control, 2 fortified samples) for analysis was approximately 2 hours. The time required for the GC analysis of a single sample was approximately 10 minutes. The duration of the analytical set

depended upon the number of samples (usually 12 plus required calibration/linearity standard runs) and was automated by auto-sample injection.

#### **Section IV. Field-Measured MITC Concentrations**

MITC field scale drizzle boom and shank concentration results (in  $\mu\text{g m}^{-3}$ ) are presented in Tables 4 and 5. Table 6 provides concentration data collected from the four W, X, Y, and Z receptor locations positioned between the two field test plots. Whole field average values are the average of the eight receptor locations from each application plot, or four in the case of the between-treatment plots W, X, Y, and Z ambient receptors. For co-located duplicate receptors (DB3, 7 and SH4, 8) the highest measured MITC concentration was used for reporting from each location. The highest measured whole field average for drizzle boom was  $417 \mu\text{g m}^{-3}$  (138 ppb) while the highest average for shank injection method was  $78 \mu\text{g m}^{-3}$  (26 ppb; see Figures 7 and 8). Drizzle boom peak concentrations were observed during the four hour sampling period post application (sample interval C, see Table 4). Shank injection MITC concentrations were observed to be highest during the 16 hour post application sampling interval (sample interval F; see Table 5). The highest averaged concentration for the four ambient W, X, Y, and Z air monitors was  $111 \mu\text{g m}^{-3}$  (37 ppb), also observed during the 16 hour post application period (see sample interval F; Table 6 and Figure 9). The maximum MITC air concentration was observed from drizzle boom four hours post application ( $963 \mu\text{g m}^{-3}$  or 318 ppb). The single maximum measured MITC air concentration for shank injection ( $122 \mu\text{g m}^{-3}$  or 40 ppb) occurred 16 hours post application (sample interval F; Table 5). Maximum measured air concentration for the four additional ambient samplers was  $228 \mu\text{g m}^{-3}$  (75 ppb) for sampler Y, also during the 16-20 hour post application sampling interval. Between 16 and 20 hours post-shank application, the measured MITC concentrations from air monitoring locations positioned equidistantly between

the two test plots indicate that directional off-field MITC emission from the drizzle boom test plot during this period may be contributing to the observed higher shank MITC emissions.

## **Section V. Field Estimated MITC Emission Rate Assessment**

To assess the potential for bystander exposure in a manner consistent with practices employed by regulatory agencies and registrants, MITC volatilization density (flux) in units mass/surface area/time together with total cumulative loss were estimated by a 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. Cal DPR Emissions Assessment Method criteria (see Appendix F) 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 > 95<sup>th</sup> percent confidence level) and the intercept term was not significant (signifying the 95<sup>th</sup> percent confidence level included the origin). If the slope was not significant or the intercept term was significant, then the least squares regression method had to be applied forcing the slope through 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. Periodically, other more conservative default factors were employed for estimation when the modeled /measured emission could not be adequately

explained by using an hourly averaged summary of wind direction over a particular period (see Period 4 in Appendix F). Following the technical procedures outline by Cal DPR's emission estimation process in Appendix F, the estimated total cumulative MITC loss by drizzle boom was calculated to be 47% compared to 12.6% by soil incorporated shank injection (total cumulative loss here assumes a 1:1 molar stoichiometry, complete conversion of metam sodium to MITC, and loss is by surface emission after application). Figure 1 illustrates the relative emission rates of drizzle boom to shank over the continuous 4-day application/post application time frame.

Drizzle Boom: It was found that drizzle boom test plot measured and modeled emission data were well ordered and usually were well correlated allowing emission rate estimation by slope. Notable exceptions were for one interval (Period 4) where a pronounced and strong wind shift occurred before the end of this monitoring period and resulted in poor measured to modeled concentration correlation (see Appendix F). For this period, the use of hourly-averaged wind direction that could not account for a sudden directional shift could explain the lack of association among receptor measured and modeled emission values. Due to poor linear correlation, the generally more conservative mean measured/mean model approach was also applied for the last four periods when low measured MITC receptor emissions likely resulted in the observed greater measured to modeled emission variation.

Soil Incorporated Shank Injection: The wind direction during the first five 4-hr air monitoring periods predominated from the Northwest from the higher upwind emission drizzle boom plot location towards the lower emission downwind shank test plot (see Figures 2 and 3). This downwind MITC contribution influenced the reliability of using a linear slope for field

measured/modeled emission flux estimation at the shank plot. As a result, shank flux estimates were generated by the generally more conservative mean measured/mean flux estimation Cal DPR approach at application and up to the first five post-application periods. The occurrence of detectable MITC concentrations at two ambient receptor locations (W and Y) located approximately equidistant between the two test plots (see Table 6 and Figure 9) further corroborated that emissions from the drizzle boom test plot enhanced MITC concentrations at the more northwesterly shank receptor locations. From the above it is reasonable to infer that MITC source contributions from the higher emission drizzle boom plot influenced the capability of relying on linear regression for estimating flux among field measured versus modeled emissions over the first five 4-hour receptor collection periods.

It is important to note that measured MITC emissions from the shank plot when compared to the drizzle boom plot were appreciably lower during and through the 4-day post application time frame (see Figures 1, 7 and 8). It is reasonable to conclude that downwind drizzle boom source contributions highly influenced shank assessment methods that rely on linear goodness of fit. To more accurately calculate emission rates from plots downwind from other treated plots, Cal DPR (2006) first generated emission rates for the upwind plots and utilizing the back calculated emission rate values, estimated MITC concentrations for downwind receptors after background subtraction. The reported emission rates in Appendix F were performed without employing background subtraction because a procedure such as employed by Cal DPR (2006) was not found to be appropriate for this data set. When defaulting to this more conservative approach, it is reasonable to anticipate over-estimation of field emission rates. This especially would be expected under circumstances where higher near-field source contributions can mask actual field emissions from lower emission applications such as at this shank injection application.

Finally, this field-scale 2008 reduced-emission application information provides regionally specific emission flux data typical of the cooler fall climatic conditions when PNW fumigations are occurring. Although emission flux was back-calculated using measured air concentrations based upon approximately 2-acre field plots, flux terms generated for this field-scale emission demonstration should be representative of field emissions from 100-200 acre field applications that typify this region. Near-field measured emissions from earlier larger field MITC bystander evaluations conducted in 2007 are complementary to observed emissions in this current report. Based on our findings, we anticipate that appreciable reductions can be realized in fumigant emissions through grower/consulting agronomist adoption of reduced emission practices. Field emission estimates and on-site field meteorological data for generating flux and cumulative MITC loss can be downloaded from <http://feql.wsu.edu/data/>.

**Table 4  
Drizzle Boom Chemigation MITC Concentrations**

<sup>1</sup> Approximate Sampler Start Date & Time	<sup>2</sup> Approximate hours post fumigation (Time interval code)	<sup>3</sup> Approx. Sample Duration (hr)	Sampler DB1 (µg/m <sup>3</sup> )	Sampler DB2 (µg/m <sup>3</sup> )	Sampler DB3-L (µg/m <sup>3</sup> )	Sampler DB3-R (µg/m <sup>3</sup> )	Sampler DB4 (µg/m <sup>3</sup> )	Sampler DB5 (µg/m <sup>3</sup> )	Sampler DB6 (µg/m <sup>3</sup> )	Sampler DB7-L (µg/m <sup>3</sup> )	Sampler DB7-R (µg/m <sup>3</sup> )	Sampler DB8 (µg/m <sup>3</sup> )
10/8/08 1:04 PM	Pre Application (A)	3:51	0.73	0.62	0.97	0.91	0.67	0.69	0.58	0.46	0.47	0.61
10/9/08 11:27 AM	Application (B)	1:46	0.61	0.77	0.67	na <sup>4</sup>	1.12	22.4	735	797	763.4	681
10/9/08 1:13 PM	4 (C)	1:42	< LOD	nd <sup>5</sup>	nd	(0.09)	71.6	216	855	949	963	811
10/9/08 2:55 PM	8 (D)	3:45	6.12	6.02	7.55	7.21	365	396	388	350	na	292
10/9/08 6:40 PM	12 (E)	3:48	47.0	81.3	62.9	62.2	239	109	89.8	131	na	213
10/9/08 10:28 PM	16 (F)	4:12	194	73.6	48.5	50.0	35.7	40.0	199	404	433	410
10/10/08 2:40 AM	20 (G)	4:30	6.75	6.50	6.15	6.41	6.93	7.27	35.7	124	131	176
10/10/08 7:10 AM	24 (H)	4:35	26.7	8.14	6.34	6.10	6.33	6.59	6.69	37.4	33.8	114
10/10/08 11:46 AM	28 (I)	4:13	119	6.93	nd	nd	< LOD	nd	nd	0.58	0.82	111
10/10/08 3:59 PM	32 (J)	2:35	70.2	(0.29)	nd	nd	nd	nd	nd	nd	nd	69.4
10/10/08 6:34 PM	36 (K)	4:06	65.5	(0.12)	< LOD	(0.09)	< LOD	< LOD	nd	< LOD	(0.07)	55.4
10/10/08 10:40 PM	40 (L)	4:16	73.8	1.35	nd	nd	nd	nd	nd	(0.15)	(0.18)	51.4
10/11/08 2:56 AM	44 (M)	4:34	15.6	2.55	2.90	3.13	2.24	1.64	2.84	17.8	16.8	52.9
10/11/08 7:30 AM	48 (N)	3:13	2.51	1.77	1.72	1.95	2.09	1.81	2.04	12.0	11.2	37.9

**Table 4 continued  
Drizzle Boom Chemigation MITC Concentrations**

<sup>1</sup> Approximate Sampler Start Date & Time	<sup>2</sup> Approximate hours post fumigation (Time interval code)	<sup>3</sup> Approx. Sample Duration (hr)	Sampler DB1 (µg/m <sup>3</sup> )	Sampler DB2 (µg/m <sup>3</sup> )	Sampler DB3-L (µg/m <sup>3</sup> )	Sampler DB3-R (µg/m <sup>3</sup> )	Sampler DB4 (µg/m <sup>3</sup> )	Sampler DB5 (µg/m <sup>3</sup> )	Sampler DB6 (µg/m <sup>3</sup> )	Sampler DB7-L (µg/m <sup>3</sup> )	Sampler DB7-R (µg/m <sup>3</sup> )	Sampler DB8 (µg/m <sup>3</sup> )
10/11/08 10:43 AM	52 (O)	4:07	30.5	0.74	failure <sup>6</sup>	0.38	0.40	0.43	(0.33)	3.32	3.86	50.9
10/11/08 2:50 PM	60 (P)	7:55	8.55	1.67	1.08	1.01	1.09	1.91	9.20	45.1	44.2	56.3
10/11/08 10:45 PM	68 (Q)	8:15	31.4	21.2	14.7	15.6	16.3	21.8	29.3	43.6	43.9	61.3
10/12/08 7:00 AM	74 (R)	8:51	10.0	nd	12.1	13.4	16.3	8.55	11.4	4.50	4.78	7.89
10/12/08 3:51 PM	82 (S)	7:00	17.4	48.5	42.2	31.3	26.5	nd	14.3	11.8	12.6	14.9
10/12/08 10:51 PM	90 (T)	8:06	25.5	33.4	29.0	28.7	10.5	21.5	9.14	9.74	9.48	17.2
10/13/08 6:57 AM	94 (U)	4:58	22.7	30.6	19.8	20.0	18.1	4.80	4.49	4.72	4.79	14.1

<sup>1</sup> Start time is the start of sampler DB1. Samplers were typically started and stopped in order, DB1-DB8.

<sup>2</sup> Hours are approximate and represent the number of hours post fumigation for the start of the sample. Actual start time, operational interval, and air flow was used to calculate air concentrations (See Appendix B Table 10).

<sup>3</sup> Sample interval is approximate. Actual start time, operational interval, and air flow was used to calculate air concentrations (See Appendix B Table 10).

<sup>4</sup> not applicable

<sup>5</sup> non detect

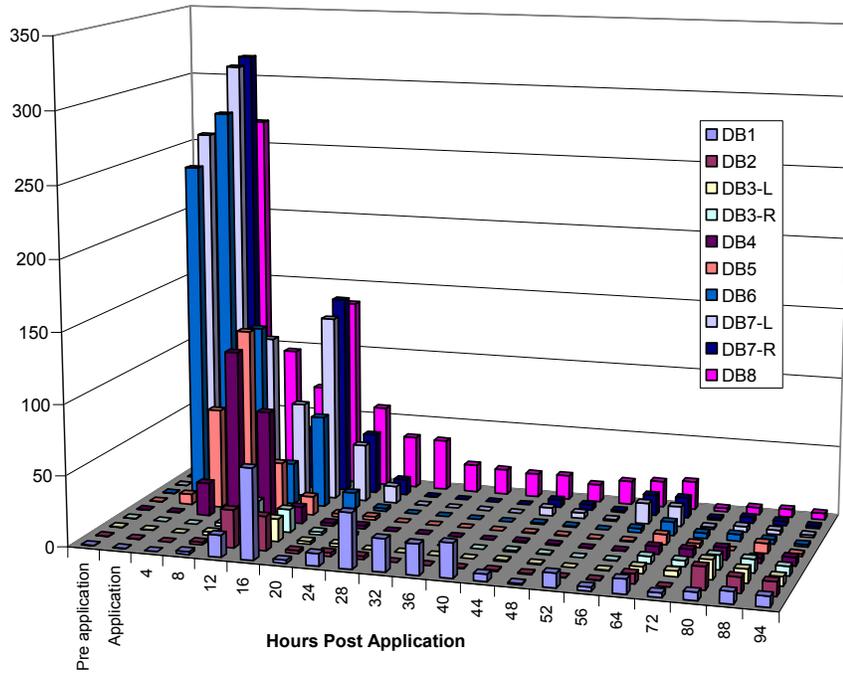
<sup>6</sup> Air sampler pump failure

<LOD= <0.07 µg/m<sup>3</sup>

Samples greater than LOD but less than LOQ are in parenthesis.

Figure 7

### MITC Emissions from Drizzle Boom Chemigation Metam Application



**Table 5  
Shank Injection MITC Concentrations**

<sup>1</sup> Approximate Sampler Start Date & Time	<sup>2</sup> Approximate hours post fumigation (Time interval code)	<sup>3</sup> Approx. Sample Duration (hr)	Sampler SH1 (µg/m <sup>3</sup> )	Sampler SH2 (µg/m <sup>3</sup> )	Sampler SH3 (µg/m <sup>3</sup> )	Sampler SH4-L (µg/m <sup>3</sup> )	Sampler SH4-R (µg/m <sup>3</sup> )	Sampler SH5 (µg/m <sup>3</sup> )	Sampler SH6 (µg/m <sup>3</sup> )	Sampler SH7 (µg/m <sup>3</sup> )	Sampler SH8-L (µg/m <sup>3</sup> )	Sampler SH8-R (µg/m <sup>3</sup> )
10/8/08 12:50 PM	Pre Application (A)	4:06	0.36	0.40	0.47	0.57	nd <sup>4</sup>	0.58	0.55	0.67	0.63	0.73
10/9/08 12:11 PM	Application (B)	0:31	1.94	2.64	4.00	12.9	12.7	21.3	10.4	8.64	14.2	15.3
10/9/08 12:45 PM	4 (C)	2:05	7.20	9.55	15.4	22.0	24.0	24.7	17.3	17.6	19.3	20.5
10/9/08 2:51 PM	8 (D)	3:49	4.74	6.44	9.12	16.6	16.5	24.2	23.7	19.6	11.5	11.6
10/9/08 6:40 PM	12 (E)	4:12	6.72	12.8	17.8	21.7	22.3	29.3	21.2	22.0	7.27	7.06
10/9/08 10:52 PM	16 (F)	3:48	36.9	61.4	81.1	89.1	72.2	122	106	50.3	76.5	57.6
10/10/08 2:40 AM	20 (G)	4:34	nd	40.3	43.9	39.1	46.1	33.4	40.5	25.1	28.1	37.3
10/10/08 7:14 AM	24 (H)	3:12	22.2	18.8	8.59	9.21	8.65	6.81	6.35	6.81	18.4	19.0
10/10/08 10:29 AM	28 (I)	4:20	10.1	12.9	1.75	0.95	1.11	0.39	(0.32)	(0.29)	4.27	4.56
10/10/08 2:53 PM	32 (J)	3:40	9.50	10.3	<LOD	nd	nd	nd	nd	nd	4.02	3.94
10/10/08 6:33 PM	36 (K)	4:08	7.87	10.6	(0.09)	(0.09)	(0.08)	nd	nd	nd	2.45	2.31
10/10/08 10:41 PM	40 (L)	4:17	6.66	8.07	<LOD	<LOD	<LOD	nd	nd	nd	1.13	1.26
10/11/08 2:58 AM	44 (M)	5:07	10.3	6.69	2.97	1.41	nd	1.15	1.12	0.98	6.60	6.40
10/11/08 8:05 AM	48 (N)	3:10	9.73	5.48	1.91	1.85	4.42	1.65	1.57	1.65	6.41	6.97

**Table 5 continued  
Shank Injection MITC Concentrations**

<sup>1</sup> Approximate Sampler Start Date & Time	<sup>2</sup> Approximate hours post fumigation (Time interval code)	<sup>3</sup> Approx. Sample Duration (hr)	Sampler SH1 (µg/m <sup>3</sup> )	Sampler SH2 (µg/m <sup>3</sup> )	Sampler SH3 (µg/m <sup>3</sup> )	Sampler SH4-L (µg/m <sup>3</sup> )	Sampler SH4-R (µg/m <sup>3</sup> )	Sampler SH5 (µg/m <sup>3</sup> )	Sampler SH6 (µg/m <sup>3</sup> )	Sampler SH7 (µg/m <sup>3</sup> )	Sampler SH8-L (µg/m <sup>3</sup> )	Sampler SH8-R (µg/m <sup>3</sup> )
10/11/08 11:15 AM	52 (O)	4:02	7.34	5.02	(0.28)	(0.23)	nd	(0.14)	(0.17)	(0.17)	3.50	3.75
10/11/08 3:17 PM	60 (P)	7:48	7.59	10.8	10.1	12.4	12.7	14.0	11.9	7.43	9.84	10.1
10/11/08 11:05 PM	68 (Q)	8:21	8.29	10.7	11.2	11.2	11.2	8.22	6.86	9.45	9.91	10.3
10/12/08 7:26 AM	74 (R)	7:25	2.14	3.09	2.60	2.82	2.88	2.52	2.69	2.05	2.13	2.26
10/12/08 2:51 PM	82 (S)	8:07	8.21	9.06	8.82	9.96	10.0	10.6	9.64	10.4	9.15	9.80
10/12/08 10:58 PM	90 (T)	8:45	5.82	7.17	5.85	5.85	6.16	6.20	5.91	7.38	6.60	7.12
10/13/08 7:43 AM	94 (U)	3:57	5.36	5.86	5.35	5.35	5.37	4.99	5.51	5.40	5.93	5.85

<sup>1</sup> Start time is the start of sampler DB1. Samplers were typically started and stopped in order, DB1-DB8.

<sup>2</sup> Hours are approximate and represent the number of hours post fumigation for the start of the sample. Actual start time, operational interval, and air flow was used to calculate air concentrations (See Appendix B Table 11).

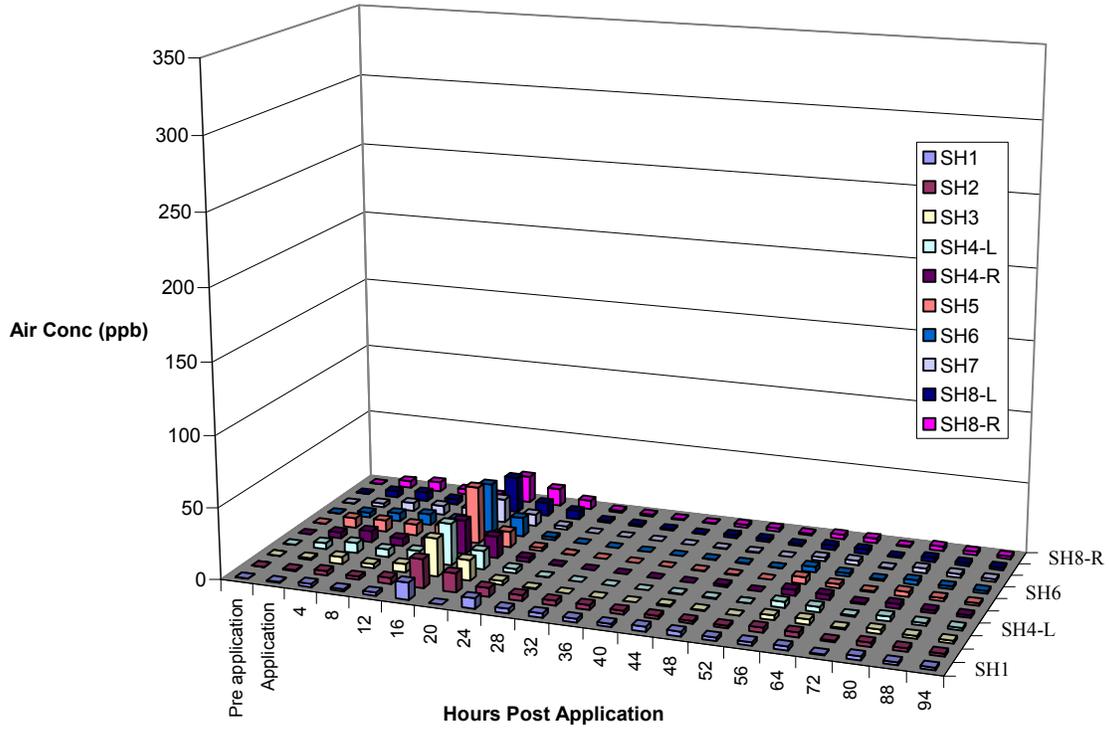
<sup>3</sup> Sample interval is approximate. Actual start time, operational interval, and air flow was used to calculate air concentrations (See Appendix B Table 11).

<sup>4</sup> non detect

<LOD= <0.07 µg/m<sup>3</sup>

Samples greater than LOD but less than LOQ are in parenthesis.

**Figure 8**  
**MITC Emissions from Shank Injection Metam Application**



**Table 6**  
**Near Treatment Plot Ambient MITC Concentrations**

<sup>1</sup> Approximate Sampler Start Date & Time	<sup>2</sup> Approximate hours post fumigation (Time interval code)	<sup>3</sup> Approx. Sample Duration (hr)	Sampler W ( $\mu\text{g}/\text{m}^3$ )	Sampler X ( $\mu\text{g}/\text{m}^3$ )	Sampler Y ( $\mu\text{g}/\text{m}^3$ )	Sampler Z ( $\mu\text{g}/\text{m}^3$ )
10/8/08 12:41 PM	Pre Application (A)	3:59	0.48	0.51	0.95	0.67
10/9/08 11:36 AM	Application (B)	1:17	11.6	17.1	115	(0.18)
10/9/08 12:54 PM	4 (C)	2:04	44.0	15.5	95.8	< LOD
10/9/08 2:58 PM	8 (D)	3:50	21.8	9.93	71.0	5.72
10/9/08 6:49 PM	12 (E)	3:55	37.9	65.9	102	12.2
10/9/08 10:45 PM	16 (F)	4:05	145	42.6	228	27.6
10/10/08 2:50 AM	20 (G)	4:42	51.2	10.6	66.9	26.1
10/10/08 7:32 AM	24 (H)	3:07	8.68	6.21	7.59	17.7
10/10/08 10:41 AM	28 (I)	4:21	0.71	< LOD	2.20	1.81
10/10/08 3:02 PM	32 (J)	3:38	(0.24)	nd <sup>4</sup>	2.90	0.86
10/10/08 6:40 PM	36 (K)	4:08	(0.28)	< LOD	1.89	0.37
10/10/08 10:48 PM	40 (L)	4:16	nd	nd	(0.27)	1.13
10/11/08 3:04 AM	44 (M)	5:11	failure <sup>5</sup>	0.93	4.42	6.38
10/11/08 8:15 AM	48 (N)	3:08	2.03	2.11	2.03	6.43
10/11/08 11:23 AM	52 (O)	4:02	0.51	0.40	2.47	2.97
10/11/08 3:25 PM	60 (P)	7:49	failure	1.98	34.8	9.66
10/11/08 11:14 PM	68 (Q)	8:18	failure	8.71	31.3	6.54
10/12/08 7:32 AM	74 (R)	7:26	2.25	1.94	1.95	2.25
10/12/08 2:58 PM	82 (S)	8:06	8.02	11.7	10.0	10.7
10/12/08 11:04 PM	90 (T)	8:09	failure	7.31	7.67	4.94
10/13/08 7:19 AM	94 (U)	4:15	2.26	4.65	4.38	5.31

<sup>1</sup> Start time is the start of sampler DB1. Samplers were typically started and stopped in order, DB1-DB8.

<sup>2</sup> Hours are approximate and represent the number of hours post fumigation for the start of the sample. Actual start time, operational interval, and air flow was used to calculate air concentrations (See Appendix B Table 12).

<sup>3</sup> Sample interval is approximate. Actual start time, operational interval, and air flow was used to calculate air concentrations (See Appendix B Table 12).

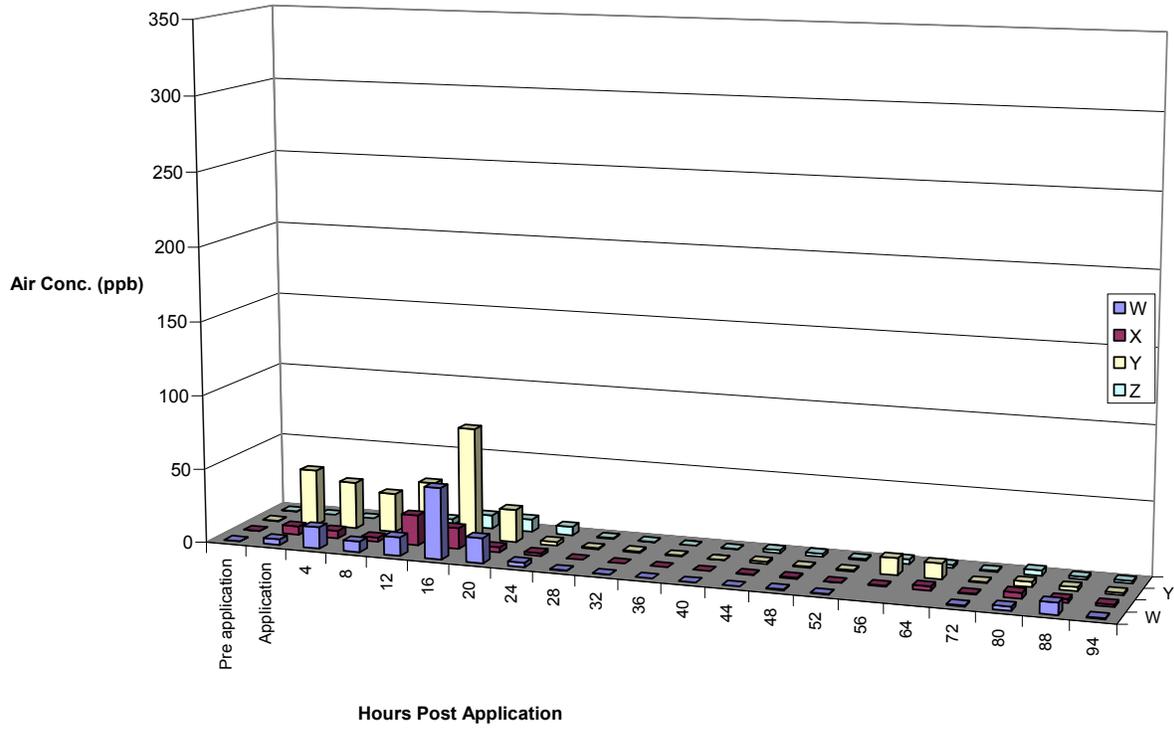
<sup>4</sup> non detect

<sup>5</sup> Air sampler pump failure

<LOD= <0.07  $\mu\text{g}/\text{m}^3$

Samples greater than LOD but less than LOQ are in parenthesis.

**Figure 9**  
**MITC Emissions from Near Plot Ambient Monitoring through 4 days Post Application**



**Table 7**  
**2008 MITC Method Validation Results**

<b>600 mg Cartridge Fortification (µg)</b>	<b>Recovery %</b>
<b>0.25</b>	92.9%
	97.5%
	93.3%
<b>25</b>	102.2%
	104.5%
	97.4%
<b>300</b>	92.3%
	107.2%
	92.9%
<b>Overall average validation recovery</b>	<b>97.8 ± 5.6%</b>

**Table 8**  
**2008 Concurrent Fortification Recovery Results**

<b>Fortification (µg)</b>	<b>Recovery Range (%)</b>	<b>Average Recovery (%)</b>
0.2	86-99%	92 ± 10% n=2
0.25	83-94%	89 ± 3% n=12
0.5	84-128%	103 ± 18% n=6
2	98-154%	120 ± 30% n=3
2.5	81-102%	92 ± 5% n=30
5	90-92%	91 ± 1% n=3
25	90-108%	97 ± 4% n=28
200	90-104%	95 ± 4% n=11
Overall average recovery 95 ± 9%, n=95		

**Table 9**  
**Field Fortification and Spiked Trip Blanks**  
**Recoveries**

Sample ID	Fortification (µg)	Air sampled (m <sup>3</sup> )	MITC Recovered (µg)	Recovery <sup>1</sup> (%)
WSU-C-101008-1	NA <sup>2</sup>	0.24 (4 hr sample)	0.52 (equivalent to 2.15 µg/m <sup>3</sup> )	NA
WSU-F-101008-1	100	0.24 (4 hr sample)	97.2	96.7
WSU-C-101108-2	NA	0.24 (4 hr sample)	0.26 (equivalent to 1.07 µg/m <sup>3</sup> )	NA
WSU-F-101108-2	100	0.24 (4 hr sample)	94.0	93.8
WSU-C-101308-3	NA	0.48 (8 hr sample)	6.8 (equivalent to 14.3 µg/m <sup>3</sup> )	NA
WSU-F-101308-3	100	0.48 (8 hr sample)	98.2	91.4
Average field spike recovery			94 ± 2.7%	
TB-100908-1	NA	NA	ND <sup>3</sup>	NA
TB-100908-2	NA	NA	ND	NA
TB-100908-3	NA	NA	ND	NA
TB-101008-4	NA	NA	ND	NA
Average trip blank recovery			ND	
SB 100908-1	100	NA		91.7
SB 100908-2	100	NA		92.9
SB 100908-3	100	NA		94.3
SB 101008-4	100	NA		98.2
SB 101008-5	100	NA		99.9
Average spike trip blank recovery			95.4 ± 3.5%	

<sup>1</sup> After subtraction of control background MITC

<sup>2</sup>NA=Not applicable

<sup>3</sup>ND= Not detected

**Appendix B  
Project Protocol**

**Field and Analytical Protocol  
Project No. FEQL-0808**

**Page 1 of 7**

**PROJECT TITLE: Measuring Off-Site Movement of MITC  
Following Shank and Modified Center Pivot  
Chemigation Applications**

**EPA TEST GUIDELINE:** This study will adhere to guidelines contained in Series 875 of the U.S. EPA Pesticide Assessment Guidelines: Occupational and Residential Exposure Test Guidelines.

**PROJECT COORDINATOR** Vincent R. Hebert:

**Organization:** Food and Environmental Quality Laboratory  
Washington State University  
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**COLLABORATION**

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**Telephone:** 509-547-9771

**Contact:** Monte Spence  
**Organization:** Wind Flow Fertilizer Inc.  
**Address:** 15030 Rd 26<sup>th</sup> SW.  
Mattawa, WA. Postal Code, 99344  
**Telephone:** 509- 932-4685

**Contact:** David Sullivan  
**Organization:** Sullivan Environmental Consulting, Inc.  
**Address:** 1900 Elkin Street, Suite 200  
Alexandria, VA 22308  
**Telephone:** 703-780-4580

**PROJECT DURATION:** September 2008 through February 2009

**PROJECT SUMMARY:**

The focus of this work plan will evaluate putative best management pre-plant fumigation application practices to reduce off-target movement. One low pressure center pivot system will be identified for applying 42% metam sodium in aqueous solution, from here referred to as metam, to two separate ca. 2 acre test plots on one circle for evaluating fumigant volatilization flux density. One test plot will receive a water run chemigation treatment application using a modified low elevation drizzle boom design that can putatively minimize airborne transport during application. At the opposing area of the field, metam will be concurrently applied at the

same rate by shank injection/soil compaction to the second test plot. This study will be designed to determine representative atmospheric emission flux of methyl isothiocyanate (MITC) pre-application, during application, and 96 hours post-application by these two application techniques. Estimating volatilization flux density will be accomplished by continuously measuring MITC air concentrations at eight sites surrounding the periphery of each plot over the experimental time-frame to back-calculate flux. Over the course of the field study, continuous meteorological measurements will be recorded in close proximity to the two treatment plots. The treatment area used in these two separate application plots should provide representative and comparative emission trends over time for full center pivot drizzle boom and shank field application events.

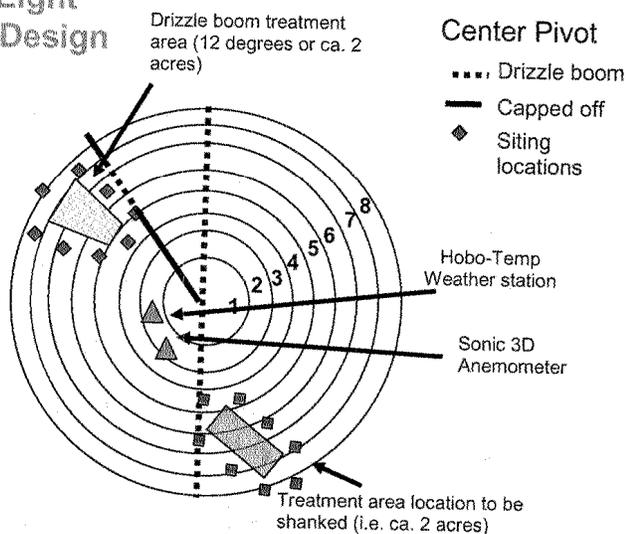
**OVERVIEW:**

In 2006 and in 2007, we observed substantial reduction in emission by shank injection when compared to conventional chemigation both during and post-application. This later observation suggests that shank injection with soil compaction (or other putative emission-reducing application practices) can significantly decrease atmospheric loss of MITC while improving product soil retention, possibly leading to reduced rates of application and thus further emission reductions to surrounding communities. Unfortunately, we were not able to conduct these earlier demonstrations in a comparative manner to best estimate MITC air emission per surface area per unit time (i.e.,  $\text{ug m}^{-2} \text{sec}^{-1}$ ; i.e., volatilization flux). This 2008 drizzle boom/shank demonstration design takes into account continuous MITC near-field emissions monitoring before, during, and through 4-days post-application. These within field test plot applications will be concurrently conducted to rule out the influence of climatic factors on observed emissions. The field work will be conducted with the assistance from Western Farm Service, and Wind Flow Inc. Sullivan Environmental Consulting, Inc. will serve in providing field meteorological instrumentation and consultation.

**APPROACH:**

Field locations: One 122 acre field crop circle (Figure 1) has been identified for this evaluation. Surface soil to a depth of ca. 25 cm will be taken within treatment plot locations for texture characterization. This pre-plant potato circle will receive enough water to bring the field to the desired soil moisture prior to metam application. The location for the drizzle boom and shank application plots will be at opposing field locations and orientated with enough separation to minimize cross-contamination concerns.

### 122 Acre Eight Tower Flux Design



Pre-application (-1 day) air sampling will be conducted at both application plots. Specific application information for both plots (i.e. weather conditions during application, rate of metam application, boom nozzle configuration, soil depth of shanking, time for completing the application, soil temperatures, and original observations) will be documented in a FIELD DATA BOOK (see below for data book requirements).

**Chemigation:** Fifty gallons per acre of metam with 0.75 to 1 inch of water will be applied by a modified "drizzle boom" center pivot chemigation assembly that uniformly lowers the application height to ca. 3 feet from the soil surface. This application will be performed in ca. six hours and be made at the standard rotational speed of ca. 6 degrees per hour. Pre-application preparation will be consistent with standard center pivot application practices. The ca. 6-hour application time (i.e. approximately 36 degree sweep), will serve as the basis to describe volatilization flux density by this application technique. Application specifics will be documented in the FIELD DATA BOOK.

**Soil-incorporated Shank Injection:** A section within the circle of similar treatment acreage will be shank injected with soil compaction at a similar rate of ca. 50 gallons per acre metam according to label requirements. This section will be orientated within the circle to reduce cross contamination. The anticipated timing for performing the shank metam application will be similar to the drizzle boom treatment above. Application specifics will be documented in the FIELD DATA BOOK.

Air Monitoring: Uniform siting procedures at the two field plots will include positioning a minimum of eight mast air samplers equidistantly 5-10 meters from the plot application edge surrounding the periphery of the application zone. A portable Hobo-Temp electronic weather station will measure wind speed, wind direction, precipitation, surface soil temperature, and ambient temperature. A 3-D sonic anemometer will also be employed by Sullivan Environmental.

MITC in near-field air will be monitored pre-application, during application, and through 4 days post-application. Pre-application air sampling will be performed to determine the extent ambient MITC vapors are present from other sources, if at all. Ambient air sampling will be established around each of the two field plots, with continuous operation during the entire pre and post fumigation air monitoring period. Sampling masts will consist of a cross-arm at approximately 2 meter height that can hold two collocated charcoal sampling cartridges (duplicate sampling events only). Each cartridge will contain 400 mg/ 200 mg Anasorb CSC, Coconut Charcoal Sorbent tubes (prepared by SKC West, Fullerton). The pump flows will be set at ca. 1 L min<sup>-1</sup>, but actual flow will be measured at the start and end of each sampling period using calibrated flow meters. Field fortifications will be routinely performed at the WSU Tri Cities campus to monitor trapping efficiency over the application and post-application sampling interval time-frame.

Sampling Frequency and Duration: The sampling masts and meteorological equipment will be operated prior to application, during application, and over a number of 4 to 8 hour sampling intervals up to 4 days post application. Air sampling at 1 L min<sup>-1</sup> will be taken at 4 hour intervals for pre-application, during application, and from time-zero through 2-days post application. Eight hour air sampling intervals will be conducted from 2 to 4 days post application. Two sites per field plot will be sampled in duplicate per interval sampling event. The sum of 420 sample events will be taken representing the two field plots, 21 air monitoring periods, and 8 samplers per plot location.

Sample Coding: The samples acquired from the field will be given a sample code that will be used to track each sample as it gathered through analysis. This code will be constructed so that each site, day, collocated duplicate, time of day and trip blanks will have unique alphanumeric values that will be traceable. The coding will be as follows:

<b>Drizzle Boom Station Site Code*</b>	<b>Interval Code**</b>	<b>Co-location</b>	<b>Code***</b>
Station 1 = DB1	A-U (21 intervals)	none	Date of sampling
Station 2 = DB2	A-U (21 intervals)	none	Date of sampling
Station 3 = DB3	A-U (21 intervals)	R/L****	Date of sampling
Station 4 = DB4	A-U (21 intervals)	none	Date of sampling
Station 5 = DB5	A-U (21 intervals)	none	Date of sampling
Station 6 = DB6	A-U (21 intervals)	none	Date of sampling
Station 7 = DB7	A-U (21 intervals)	R/L	Date of sampling
Station 8 = DB8	A-U (21 intervals)	none	Date of sampling
<b>Shank Station Site Code*</b>	<b>Interval Code**</b>	<b>Co-location</b>	<b>Code***</b>
Station 1 = SH1	A-U (21 intervals)	none	Date of sampling
Station 2 = SH2	A-U (21 intervals)	none	Date of sampling

Station 3 = SH3	A-U (21 intervals)	none	Date of sampling
Station 4 = SH4	A-U (21 intervals)	R/L	Date of sampling
Station 5 = SH5	A-U (21 intervals)	none	Date of sampling
Station 6 = SH6	A-U (21 intervals)	none	Date of sampling
Station 7 = SH7	A-U (21 intervals)	none	Date of sampling
Station 8 = SH8	A-U (21 intervals)	R/L	Date of sampling

- \* Station locations will be kept confidential.
- \*\* May be modified if sampling interval is delayed by weather conditions
- \*\*\* Date of acquired field air sample
- \*\*\*\* R/L; Co-located activated charcoal cartridge sampling

The WSU-FEQL will attempt to conduct concurrent sampling events at both the chemigation and shank injection field locations. However, application timing and other factors such as pre-watering may result in a lag in sampling times between the two plot locations. Treatment blanks will accompany each shipment over ca. 4 day air sampling period and will receive a TB designation.

A typical event for Shank Station # 6 on the completion of the sixth sampling interval if performed on October 24<sup>th</sup>, 2008 would receive a coding **SH6-F-102408**. Two stations at each field plot location will have co-located samples. In all cases, co-located samples will be taken from the left side of the mast and will have the D (duplicate) code right after the station site code. A charcoal tube labeled **DB3D-A-102008** would uniquely identify the left co-located air sample taken at station 3 on October 20<sup>th</sup>, 2008 during the first sampling period, DB3-A-102008 would be the regular sample from the same period. A charcoal tube labeled **SHTB-B-102008** would indicate that the sample is a trip blank stored with the shank samples taken on October 20<sup>th</sup>, 2008 during the second sampling period. A sample labeled **F-D-R-102008** would indicate a field fortification (F) at the WSU-TC campus taken on October 20, 2008 from the right co-located sampling position during the fourth sampling period.

Sample Handling and Quality Control: At the end of each sampling period, the sampling media will be capped and labeled uniquely identifying the individual sample. The samples will be transported to the WSU Food and Environmental Quality Laboratory on blue ice and stored at -80° C prior to analysis. Trip blanks (i.e., no MITC) and chain of custody documentation will accompany each sample shipment. Spiked trip blanks (cartridges fortified with a known amount of MITC) will also routinely accompany sample shipments to verify analyte stability.

Fortified spikes will be made to the intakes of the air sampling tubes during the period of air monitoring. These tubes will be run outdoors at the WSU-Tri Cities campus for 4 hours during the pre to early post-application period and for 8 hours during the longer air sampling post-application periods to verify quantitative field recovery of vapor-trapped MITC.

Laboratory Analysis: The Food and Environmental Quality Laboratory (FEQL) is a regulatory science 40 CFR Part 160 Good Laboratory Practices (GLP) facility under the direction of Dr. Hebert. Although the analytical facility will follow all internal regulatory science procedures, this evaluation can not be performed under strict GLP requirements since the field phase will not be conducted under GLP. Extraction and analytical methods to be used in this evaluation have been previously validated by the analysts performing the work. The Lab will employ a previously validated solvent elution method that uses an 80:20 v/v mixture of ethyl

acetate/carbon disulfide for extracting MITC from charcoal air sampling tubes (FEQL, 2006). MITC in the solvent extract will be determined using gas chromatography with nitrogen-phosphorus thermionic specific detection. All steps will be taken to insure sample integrity on an analytical set-by-set basis (i.e., controls, fortifications, calibrations, and linearities). The generated data will be expressed in units of mass per volume air ( $\mu\text{g m}^{-3}$ ) taken over the sampling interval for assessing near-field air residues.

Breakthrough: A breakthrough evaluation has been previously conducted that demonstrates quantitative recovery over the maximum eight hour air sampling period for the 400 mg/ 200 mg Anasorb CSC, Coconut Charcoal sorbent cartridges at temperatures expected during the application event (FEQL, 2008).

Storage Stability: An 85-day frozen storage stability study has been previously conducted by the WSU-FEQL (FEQL, 2006). It is anticipated that all sample analyses will be completed before the established 85-day storage stability period.

Statistical Method: Criteria for acceptance of standard curve(s) or other statistical methods shall be determined by the Project Coordinator and documented in the raw data.

Field Documentation and Record Keeping: All operations, data and observations appropriate to this study should be recorded directly and promptly into the FIELD DATA BOOK. General instructions for completion of the field data book can be found in this book. This data book was designed for collecting field information and serves as an authentic record of fieldwork. It has six parts or chapters containing the following information:

<u>PART</u>	<u>SUBJECT</u>
1	Personnel Log
2	Communications/ Field Chronological Log and Notes
3	Field Trial Site Information/Placement of Air Samplers
4	Air Sampler Calibration/Field Testing Data Sheets
5	Air Sampler Shipping Information
6	Meteorological Records

Laboratory Documentation and Record Keeping: All operations, data, and observations shall be recorded in the laboratory write-ups sheets and log books, which must be signed and dated on date of entry. At a minimum, collect and maintain the following raw data:

- Analytical standard(s) receipt, use and disposition records
- Analytical standard(s) storage conditions
- Analytical standard(s) dilution calculations and preparation records
- Sample storage conditions and locations
- Calculation work sheets
- All chromatograms, including those which are not reported
- Chain of custody records
- Name of personnel conducting specific research functions
- Sample analysis laboratory write-ups sheets

## APPENDIX C: Sample Inventory

**Table 10**  
**Drizzle Boom MITC Samples**

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
DB1-A-100808	10/8/08 1:04 PM	10/8/08 4:55 PM	0.95	10/8/2008	12/2/2008
DB2-A-100808	10/8/08 1:02 PM	10/8/08 5:10 PM	0.95	10/8/2008	12/2/2008
DB3-A-L-100808	10/8/08 1:00 PM	10/8/08 5:07 PM	0.95	10/8/2008	12/2/2008
DB3-A-R-100808	10/8/08 1:00 PM	10/8/08 5:07 PM	0.95	10/8/2008	12/2/2008
DB4-A-100808	10/8/08 12:58 PM	10/8/08 5:04 PM	0.95	10/8/2008	12/2/2008
DB5-A-100808	10/8/08 12:58 PM	10/8/08 5:00 PM	0.95	10/8/2008	12/2/2008
DB6-A-100808	10/8/08 12:53 PM	10/8/08 4:48 PM	1	10/8/2008	12/2/2008
DB7-A-L-100808	10/8/08 12:51 PM	10/8/08 4:56 PM	1	10/8/2008	12/2/2008
DB7-A-R-100808	10/8/08 12:51 PM	10/8/08 4:56 PM	1	10/8/2008	12/2/2008
DB8-A-100808	10/8/08 1:06 PM	10/8/08 5:15 PM	0.95	10/8/2008	12/2/2008
DB1-B-100908	10/9/08 11:27 AM	10/9/08 1:13 PM	0.95	10/10/2008	11/29/2008
DB2-B-100908	10/9/08 11:29 AM	10/9/08 1:16 PM	1	10/10/2008	11/29/2008
DB3-B-L-100908	10/9/08 11:30 AM	10/9/08 1:19 PM	1.05	10/10/2008	11/29/2008
DB3-B-R-100908	10/9/08 11:30 AM	10/9/08 1:19 PM	1	10/10/2008	11/29/2008
DB4-B-100908	10/9/08 11:31 AM	10/9/08 1:24 PM	1	10/10/2008	11/29/2008
DB5-B-100908	10/9/08 11:31 AM	10/9/08 1:28 PM	1	10/10/2008	11/29/2008
DB6-B-100908	10/9/08 11:30 AM	10/9/08 1:30 PM	1	10/10/2008	11/29/2008
DB7-B-L-100908	10/9/08 11:29 AM	10/9/08 1:33 PM	1	10/10/2008	11/29/2008
DB7-B-R-100908	10/9/08 11:29 AM	10/9/08 1:33 PM	1	10/10/2008	11/29/2008
DB8-B-100908	10/9/08 11:27 AM	10/9/08 1:36 PM	1	10/10/2008	11/29/2008
DB1-C-100908	10/9/08 1:13 PM	10/9/08 2:55 PM	1	10/10/2008	11/28/2008
DB2-C-100908	10/9/08 1:16 PM	10/9/08 2:58 PM	1	10/10/2008	11/28/2008
DB3-C-L-100908	10/9/08 1:20 PM	10/9/08 2:59 PM	1.05	10/10/2008	11/28/2008
DB3-C-R-100908	10/9/08 1:20 PM	10/9/08 2:59 PM	1	10/10/2008	11/28/2008
DB4-C-100908	10/9/08 1:24 PM	10/9/08 3:02 PM	1.05	10/10/2008	11/28/2008
DB5-C-100908	10/9/08 1:28 PM	10/9/08 3:05 PM	1	10/10/2008	11/28/2008
DB6-C-100908	10/9/08 1:30 PM	10/9/08 3:06 PM	1	10/10/2008	11/28/2008
DB7-C-L-100908	10/9/08 1:33 PM	10/9/08 3:10 PM	1	10/10/2008	11/28/2008
DB7-C-R-100908	10/9/08 1:33 PM	10/9/08 3:10 PM	1	10/10/2008	11/28/2008
DB8-C-100908	10/9/08 1:36 PM	10/9/08 3:12 PM	1.05	10/10/2008	11/28/2008
DB1-D-100908	10/9/08 2:55 PM	10/9/08 6:40 PM	1	10/10/2008	11/21/2008
DB2-D-100908	10/9/08 2:58 PM	10/9/08 6:43 PM	1	10/10/2008	11/21/2008
DB3-D-L-100908	10/9/08 2:59 PM	10/9/08 6:45 PM	1.05	10/10/2008	11/21/2008
DB3-D-R-100908	10/9/08 2:59 PM	10/9/08 6:45 PM	1.05	10/10/2008	11/21/2008
DB4-D-100908	10/9/08 3:02 PM	10/9/08 6:50 PM	1	10/10/2008	11/21/2008
DB5-D-100908	10/9/08 3:05 PM	10/9/08 6:55 PM	1	10/10/2008	11/21/2008
DB6-D-100908	10/9/08 3:06 PM	10/9/08 6:57 PM	1	10/10/2008	11/21/2008
DB7-D-L-100908	10/9/08 3:10 PM	10/9/08 7:02 PM	1	10/10/2008	11/21/2008
DB7-D-R-100908	10/9/08 3:10 PM	10/9/08 7:02 PM	1	10/10/2008	11/21/2008
DB8-D-100908	10/9/08 3:12 PM	10/9/08 7:05 PM	1	10/10/2008	11/21/2008
DB1-E-100908	10/9/08 6:40 PM	10/9/08 10:28 PM	1	10/10/2008	11/18/2008

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
DB2-E-100908	10/9/08 6:43 PM	10/9/08 10:31 PM	1	10/10/2008	11/18/2008
DB3-E-L-100908	10/9/08 6:45 PM	10/9/08 10:37 PM	1.05	10/10/2008	11/18/2008
DB3-E-R-100908	10/9/08 6:45 PM	10/9/08 10:37 PM	1.1	10/10/2008	11/18/2008
DB4-E-100908	10/9/08 6:50 PM	10/9/08 10:40 PM	1	10/10/2008	11/18/2008
DB5-E-100908	10/9/08 6:55 PM	10/9/08 10:45 PM	1	10/10/2008	11/18/2008
DB6-E-100908	10/9/08 6:57 PM	10/9/08 10:48 PM	1	10/10/2008	11/18/2008
DB7-E-L-100908	10/9/08 7:02 PM	10/9/08 10:51 PM	1	10/10/2008	11/18/2008
DB7-E-R-100908	10/9/08 7:02 PM	10/9/08 10:51 PM	1	10/10/2008	11/18/2008
DB8-E-100908	10/9/08 7:05 PM	10/9/08 10:54 PM	1	10/10/2008	11/18/2008
DB1-F-100908	10/9/08 10:28 PM	10/10/08 2:40 AM	1	10/10/2008	11/17/2008
DB2-F-100908	10/9/08 10:31 PM	10/10/08 2:43 AM	1	10/10/2008	11/17/2008
DB3-F-L-100908	10/9/08 10:37 PM	10/10/08 2:45 AM	1.1	10/10/2008	11/17/2008
DB3-F-R-100908	10/9/08 10:37 PM	10/10/08 2:45 AM	1.1	10/10/2008	11/17/2008
DB4-F-100908	10/9/08 10:40 PM	10/10/08 2:48 AM	1	10/10/2008	11/17/2008
DB5-F-100908	10/9/08 10:45 PM	10/10/08 2:54 AM	1	10/10/2008	11/17/2008
DB6-F-100908	10/9/08 10:48 PM	10/10/08 2:56 AM	1	10/10/2008	11/17/2008
DB7-F-L-100908	10/9/08 10:51 PM	10/10/08 2:59 AM	1	10/10/2008	11/17/2008
DB7-F-R-100908	10/9/08 10:51 PM	10/10/08 2:59 AM	1	10/10/2008	11/17/2008
DB8-F-100908	10/9/08 10:54 PM	10/10/08 3:01 AM	1	10/10/2008	11/17/2008
DB1-G-101008	10/10/08 2:40 AM	10/10/08 7:10 AM	1.05	10/10/2008	11/16/2008
DB2-G-101008	10/10/08 2:43 AM	10/10/08 7:11 AM	1	10/10/2008	11/16/2008
DB3-G-L-101008	10/10/08 2:45 AM	10/10/08 7:14 AM	1.15	10/10/2008	11/16/2008
DB3-G-R-101008	10/10/08 2:45 AM	10/10/08 7:14 AM	1.1	10/10/2008	11/16/2008
DB4-G-101008	10/10/08 2:48 AM	10/10/08 7:17 AM	1.05	10/10/2008	11/16/2008
DB5-G-101008	10/10/08 2:54 AM	10/10/08 7:20 AM	1	10/10/2008	11/16/2008
DB6-G-101008	10/10/08 2:56 AM	10/10/08 7:22 AM	1.05	10/10/2008	11/16/2008
DB7-G-L-101008	10/10/08 2:59 AM	10/10/08 7:26 AM	1	10/10/2008	11/16/2008
DB7-G-R-101008	10/10/08 2:59 AM	10/10/08 7:26 AM	1	10/10/2008	11/16/2008
DB8-G-101008	10/10/08 3:01 AM	10/10/08 7:29 AM	1.05	10/10/2008	11/16/2008
DB1-H-101008	10/10/08 7:10 AM	10/10/08 11:45 AM	1.1	10/13/2008	11/15/2008
DB2-H-101008	10/10/08 7:11 AM	10/10/08 11:43 AM	1.05	10/13/2008	11/15/2008
DB3-H-L-101008	10/10/08 7:14 AM	10/10/08 11:39 AM	1.15	10/13/2008	11/15/2008
DB3-H-R-101008	10/10/08 7:14 AM	10/10/08 11:39 AM	1.15	10/13/2008	11/15/2008
DB4-H-101008	10/10/08 7:17 AM	10/10/08 11:33 AM	1.15	10/13/2008	11/15/2008
DB5-H-101008	10/10/08 7:20 AM	10/10/08 11:31 AM	1	10/13/2008	11/15/2008
DB6-H-101008	10/10/08 7:22 AM	10/10/08 11:28 AM	1.05	10/13/2008	11/15/2008
DB7-H-L-101008	10/10/08 7:26 AM	10/10/08 11:26 AM	1.05	10/13/2008	11/15/2008
DB7-H-R-101008	10/10/08 7:26 AM	10/10/08 11:26 AM	1.05	10/13/2008	11/15/2008
DB8-H-101008	10/10/08 7:29 AM	10/10/08 11:50 AM	1.15	10/13/2008	11/15/2008
DB1-I-101008	10/10/08 11:46 AM	10/10/08 3:59 PM	1.05	10/13/2008	11/13/2008
DB2-I-101008	10/10/08 11:43 AM	10/10/08 3:57 PM	1.05	10/13/2008	11/13/2008
DB3-I-L-101008	10/10/08 11:41 AM	10/10/08 3:54 PM	1	10/13/2008	11/13/2008
DB3-I-R-101008	10/10/08 11:41 AM	10/10/08 3:54 PM	1.1	10/13/2008	11/13/2008
DB4-I-101008	10/10/08 11:35 AM	10/10/08 3:51 PM	1.1	10/13/2008	11/13/2008
DB5-I-101008	10/10/08 11:31 AM	10/10/08 3:49 PM	1.1	10/13/2008	11/13/2008
DB6-I-101008	10/10/08 11:28 AM	10/10/08 3:47 PM	1.1	10/13/2008	11/13/2008

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
DB7-I-L-101008	10/10/08 11:26 AM	10/10/08 3:45 PM	1.05	10/13/2008	11/13/2008
DB7-I-R-101008	10/10/08 11:26 AM	10/10/08 3:45 PM	1.05	10/13/2008	11/13/2008
DB8-I-101008	10/10/08 11:50 AM	10/10/08 4:01 PM	1	10/13/2008	11/13/2008
DB1-J-101008	10/10/08 3:59 PM	10/10/08 6:34 PM	1.05	10/13/2008	11/12/2008
DB2-J-101008	10/10/08 3:57 PM	10/10/08 6:37 PM	1	10/13/2008	11/12/2008
DB3-J-L-101008	10/10/08 3:54 PM	10/10/08 6:40 PM	1	10/13/2008	11/12/2008
DB3-J-R-101008	10/10/08 3:54 PM	10/10/08 6:40 PM	1.05	10/13/2008	11/12/2008
DB4-J-101008	10/10/08 3:51 PM	10/10/08 6:41 PM	1.05	10/13/2008	11/12/2008
DB5-J-101008	10/10/08 3:49 PM	10/10/08 6:43 PM	1.05	10/13/2008	11/12/2008
DB6-J-101008	10/10/08 3:47 PM	10/10/08 6:46 PM	1.05	10/13/2008	11/12/2008
DB7-J-L-101008	10/10/08 3:45 PM	10/10/08 6:51 PM	1.05	10/13/2008	11/12/2008
DB7-J-R-101008	10/10/08 3:45 PM	10/10/08 6:51 PM	1.05	10/13/2008	11/12/2008
DB8-J-101008	10/10/08 4:01 PM	10/10/08 6:53 PM	1	10/13/2008	11/12/2008
DB1-K-101008	10/10/08 6:34 PM	10/10/08 10:40 PM	1	10/13/2008	11/9/2008
DB2-K-101008	10/10/08 6:37 PM	10/10/08 10:42 PM	1	10/13/2008	11/9/2008
DB3-K-L-101008	10/10/08 6:40 PM	10/10/08 10:44 PM	1	10/13/2008	11/9/2008
DB3-K-R-101008	10/10/08 6:40 PM	10/10/08 10:44 PM	1	10/13/2008	11/9/2008
DB4-K-101008	10/10/08 6:41 PM	10/10/08 10:47 PM	1	10/13/2008	11/9/2008
DB5-K-101008	10/10/08 6:43 PM	10/10/08 10:52 PM	1	10/13/2008	11/9/2008
DB6-K-101008	10/10/08 6:46 PM	10/10/08 10:54 PM	1	10/13/2008	11/9/2008
DB7-K-L-101008	10/10/08 6:51 PM	10/10/08 10:57 PM	1	10/13/2008	11/9/2008
DB7-K-R-101008	10/10/08 6:51 PM	10/10/08 10:57 PM	1	10/13/2008	11/9/2008
DB8-K-101008	10/10/08 6:53 PM	10/10/08 11:00 PM	1	10/13/2008	11/9/2008
DB1-L-101008	10/10/08 10:40 PM	10/11/08 2:56 AM	1	10/13/2008	11/6/2008
DB2-L-101008	10/10/08 10:42 PM	10/11/08 2:59 AM	1	10/13/2008	11/6/2008
DB3-L-L-101008	10/10/08 10:44 PM	10/11/08 3:02 AM	1	10/13/2008	11/6/2008
DB3-L-R-101008	10/10/08 10:44 PM	10/11/08 3:02 AM	1	10/13/2008	11/6/2008
DB4-L-101008	10/10/08 10:47 PM	10/11/08 3:06 AM	1	10/13/2008	11/6/2008
DB5-L-101008	10/10/08 10:52 PM	10/11/08 3:09 AM	1	10/13/2008	11/6/2008
DB6-L-101008	10/10/08 10:54 PM	10/11/08 3:12 AM	1	10/13/2008	11/6/2008
DB7-L-L-101008	10/10/08 10:57 PM	10/11/08 3:15 AM	1	10/13/2008	11/6/2008
DB7-L-R-101008	10/10/08 10:57 PM	10/11/08 3:15 AM	1	10/13/2008	11/6/2008
DB8-L-101008	10/10/08 11:00 PM	10/11/08 3:18 AM	1	10/13/2008	11/6/2008
DB1-M-101108	10/11/08 2:56 AM	10/11/08 7:30 AM	1	10/13/2008	11/4/2008
DB2-M-101108	10/11/08 2:59 AM	10/11/08 7:33 AM	1	10/13/2008	11/4/2008
DB3-M-L-101108	10/11/08 3:02 AM	10/11/08 7:36 AM	1	10/13/2008	11/4/2008
DB3-M-R-101108	10/11/08 3:02 AM	10/11/08 7:39 AM	1	10/13/2008	11/4/2008
DB4-M-101108	10/11/08 3:06 AM	10/11/08 7:41 AM	1	10/13/2008	11/4/2008
DB5-M-101108	10/11/08 3:09 AM	10/11/08 7:42 AM	1	10/13/2008	11/4/2008
DB6-M-101108	10/11/08 3:12 AM	10/11/08 7:44 AM	1	10/13/2008	11/4/2008
DB7-M-L-101108	10/11/08 3:15 AM	10/11/08 7:49 AM	1	10/13/2008	11/4/2008
DB7-M-R-101108	10/11/08 3:15 AM	10/11/08 7:49 AM	1	10/13/2008	11/4/2008
DB8-M-101108	10/11/08 3:18 AM	10/11/08 7:28 AM	1	10/13/2008	11/4/2008
DB1-N-101108	10/11/08 7:30 AM	10/11/08 10:43 AM	1	10/13/2008	11/5/2008
DB2-N-101108	10/11/08 7:33 AM	10/11/08 10:44 AM	1	10/13/2008	11/5/2008
DB3-N-L-101108	10/11/08 7:36 AM	10/11/08 10:46 AM	1	10/13/2008	11/5/2008

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
DB3-N-R-101108	10/11/08 7:39 AM	10/11/08 10:46 AM	1	10/13/2008	11/5/2008
DB4-N-101108	10/11/08 7:41 AM	10/11/08 10:48 AM	1	10/13/2008	11/5/2008
DB5-N-101108	10/11/08 7:42 AM	10/11/08 10:51 AM	1	10/13/2008	11/5/2008
DB6-N-101108	10/11/08 7:44 AM	10/11/08 10:40 AM	1	10/13/2008	11/5/2008
DB7-N-L-101108	10/11/08 7:49 AM	10/11/08 10:55 AM	1	10/13/2008	11/5/2008
DB7-N-R-101108	10/11/08 7:49 AM	10/11/08 10:55 AM	1	10/13/2008	11/5/2008
DB8-N-101108	10/11/08 7:28 AM	10/11/08 10:41 AM	1	10/13/2008	11/5/2008
DB1-O-101108	10/11/08 10:43 AM	10/11/08 2:50 PM	0.95	10/13/2008	10/30/2008
DB2-O-101108	10/11/08 10:44 AM	10/11/08 2:52 PM	1	10/13/2008	10/30/2008
DB3-O-L-101108 <sup>+</sup>	10/11/08 10:46 AM	10/11/08 2:54 PM	failure	10/13/2008	10/30/2008
DB3-O-R-101108	10/11/08 10:46 AM	10/11/08 2:54 PM	1	10/13/2008	10/30/2008
DB4-O-101108	10/11/08 10:48 AM	10/11/08 2:59 PM	1	10/13/2008	10/30/2008
DB5-O-101108	10/11/08 10:51 AM	10/11/08 3:02 PM	1	10/13/2008	10/30/2008
DB6-O-101108	10/11/08 10:40 AM	10/11/08 3:03 PM	1	10/13/2008	10/30/2008
DB7-O-L-101108	10/11/08 10:55 AM	10/11/08 2:44 PM	1	10/13/2008	10/30/2008
DB7-O-R-101108	10/11/08 10:55 AM	10/11/08 2:44 PM	1	10/13/2008	10/30/2008
DB8-O-101108	10/11/08 10:41 AM	10/11/08 2:46 PM	0.95	10/13/2008	10/30/2008
DB1-P-101108	10/11/08 2:50 PM	10/11/08 10:45 PM	0.9	10/13/2008	11/3/2008
DB2-P-101108	10/11/08 2:52 PM	10/11/08 10:47 PM	1	10/13/2008	11/3/2008
DB3-P-L-101108	10/11/08 2:54 PM	10/11/08 10:49 PM	1	10/13/2008	11/3/2008
DB3-P-R-101108	10/11/08 2:54 PM	10/11/08 10:49 PM	1	10/13/2008	11/3/2008
DB4-P-101108	10/11/08 2:59 PM	10/11/08 10:52 PM	1	10/13/2008	11/3/2008
DB5-P-101108	10/11/08 3:02 PM	10/11/08 10:55 PM	1	10/13/2008	11/3/2008
DB6-P-101108	10/11/08 3:03 PM	10/11/08 10:56 PM	1	10/13/2008	11/3/2008
DB7-P-L-101108	10/11/08 2:44 PM	10/11/08 10:42 PM	1	10/13/2008	11/3/2008
DB7-P-R-101108	10/11/08 2:44 PM	10/11/08 10:42 PM	1	10/13/2008	11/3/2008
DB8-P-101108	10/11/08 2:46 PM	10/11/08 10:43 PM	0.9	10/13/2008	11/3/2008
DB1-Q-101108	10/11/08 10:45 PM	10/12/08 7:00 AM	0.9	10/13/2008	10/27/2008
DB2-Q-101108	10/11/08 10:47 PM	10/12/08 7:02 AM	0.95	10/13/2008	10/27/2008
DB3-Q-L-101108	10/11/08 10:49 PM	10/12/08 7:04 AM	0.95	10/13/2008	10/27/2008
DB3-Q-R-101108	10/11/08 10:49 PM	10/12/08 7:04 AM	0.95	10/13/2008	10/27/2008
DB4-Q-101108	10/11/08 10:52 PM	10/12/08 7:08 AM	1	10/13/2008	10/27/2008
DB5-Q-101108	10/11/08 10:55 PM	10/12/08 7:10 AM	1	10/13/2008	10/27/2008
DB6-Q-101108	10/11/08 10:56 PM	10/12/08 7:11 AM	0.95	10/13/2008	10/27/2008
DB7-Q-L-101108	10/11/08 10:42 PM	10/12/08 6:51 AM	0.95	10/13/2008	10/27/2008
DB7-Q-R-101108	10/11/08 10:42 PM	10/12/08 6:51 AM	0.95	10/13/2008	10/27/2008
DB8-Q-101108	10/11/08 10:43 PM	10/12/08 6:54 AM	0.9	10/13/2008	10/27/2008
DB1-R-1012108	10/12/08 7:00 AM	10/12/08 3:51 PM	1	10/13/2008	10/26/2008
DB2-R-1012108	10/12/08 7:02 AM	10/12/08 3:50 PM	0.95	10/13/2008	10/26/2008
DB3-R-L-1012108	10/12/08 7:04 AM	10/12/08 3:48 PM	0.95	10/13/2008	10/26/2008
DB3-R-R-1012108	10/12/08 7:04 AM	10/12/08 3:48 PM	0.85	10/13/2008	10/26/2008
DB4-R-1012108	10/12/08 7:08 AM	10/12/08 3:45 PM	1.05	10/13/2008	10/26/2008
DB5-R-1012108	10/12/08 7:10 AM	10/12/08 3:42 PM	1	10/13/2008	10/26/2008
DB6-R-1012108	10/12/08 7:11 AM	10/12/08 3:41 PM	0.95	10/13/2008	10/26/2008
DB7-R-L-1012108	10/12/08 6:51 AM	10/12/08 3:37 PM	1	10/13/2008	10/26/2008
DB7-R-R-1012108	10/12/08 6:51 AM	10/12/08 3:37 PM	0.95	10/13/2008	10/26/2008

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
DB8-R-1012108	10/12/08 6:54 AM	10/12/08 3:52 PM	0.95	10/13/2008	10/26/2008
DB1-S-101208	10/12/08 3:51 PM	10/12/08 10:51 PM	1.1	10/13/2008	10/23/2008
DB2-S-101208	10/12/08 3:50 PM	10/12/08 10:50 PM	1.1	10/13/2008	10/23/2008
DB3-S-L-101208	10/12/08 3:48 PM	10/12/08 10:48 PM	1	10/13/2008	10/23/2008
DB3-S-R-101208	10/12/08 3:48 PM	10/12/08 10:48 PM	0.85	10/13/2008	10/23/2008
DB4-S-101208	10/12/08 3:45 PM	10/12/08 10:41 PM	1.1	10/13/2008	10/23/2008
DB5-S-101208	10/12/08 3:42 PM	10/12/08 10:38 PM	1.05	10/13/2008	10/23/2008
DB6-S-101208	10/12/08 3:41 PM	10/12/08 10:37 PM	1	10/13/2008	10/23/2008
DB7-S-L-101208	10/12/08 3:37 PM	10/12/08 10:36 PM	1.05	10/13/2008	10/23/2008
DB7-S-R-101208	10/12/08 3:37 PM	10/12/08 10:36 PM	1.05	10/13/2008	10/23/2008
DB8-S-101208	10/12/08 3:52 PM	10/12/08 10:53 PM	1	10/13/2008	10/23/2008
DB1-T-101208	10/12/08 10:51 PM	10/13/08 6:57 AM	1.05	10/13/2008	10/21/2008
DB2-T-101208	10/12/08 10:50 PM	10/13/08 6:59 AM	1.1	10/13/2008	10/21/2008
DB3-T-L-101208	10/12/08 10:48 PM	10/13/08 7:02 AM	1.1	10/13/2008	10/21/2008
DB3-T-R-101208	10/12/08 10:48 PM	10/13/08 7:02 AM	1.05	10/13/2008	10/21/2008
DB4-T-101208	10/12/08 10:41 PM	10/13/08 7:03 AM	1.1	10/13/2008	10/21/2008
DB5-T-101208	10/12/08 10:38 PM	10/13/08 7:05 AM	1.05	10/13/2008	10/21/2008
DB6-T-101208	10/12/08 10:37 PM	10/13/08 7:07 AM	1	10/13/2008	10/21/2008
DB7-T-L-101208	10/12/08 10:36 PM	10/13/08 7:09 AM	1.1	10/13/2008	10/21/2008
DB7-T-R-101208	10/12/08 10:36 PM	10/13/08 7:09 AM	1.1	10/13/2008	10/21/2008
DB8-T-101208	10/12/08 10:53 PM	10/13/08 6:55 AM	0.95	10/13/2008	10/21/2008
DB1-U-101308	10/13/08 6:57 AM	10/13/08 11:55 AM	1	10/13/2008	10/20/2008
DB2-U-101308	10/13/08 6:59 AM	10/13/08 11:56 AM	1.1	10/13/2008	10/20/2008
DB3-U-L-101308	10/13/08 7:02 AM	10/13/08 11:57 AM	1.1	10/13/2008	10/20/2008
DB3-U-R-101308	10/13/08 7:02 AM	10/13/08 11:57 AM	1	10/13/2008	10/20/2008
DB4-U-101308	10/13/08 7:03 AM	10/13/08 11:59 AM	1.1	10/13/2008	10/20/2008
DB5-U-101308	10/13/08 7:05 AM	10/13/08 12:01 PM	1.05	10/13/2008	10/20/2008
DB6-U-101308	10/13/08 7:07 AM	10/13/08 12:02 PM	1.05	10/13/2008	10/20/2008
DB7-U-L-101308	10/13/08 7:09 AM	10/13/08 12:04 PM	1.1	10/13/2008	10/20/2008
DB7-U-R-101308	10/13/08 7:09 AM	10/13/08 12:04 PM	1.1	10/13/2008	10/20/2008
DB8-U-101308	10/13/08 6:55 AM	10/13/08 12:05 PM	1	10/13/2008	10/20/2008

<sup>a</sup> The air sample pump failed on these samples.

**Table 11**  
**Shank Injection MITC Samples**

<b>Sample ID</b>	<b>Air sampler start time</b>	<b>Air sampler end time</b>	<b>Average flow rate (L/min)</b>	<b>Date transferred to -80°C</b>	<b>Date of extraction</b>
SH1-A-100808	10/8/08 12:50 PM	10/8/08 4:56 PM	1	10/8/2008	11/30/2008
SH2-A-100808	10/8/08 12:51 PM	10/8/08 4:55 PM	1	10/8/2008	11/30/2008
SH3-A-100808	10/8/08 12:53 PM	10/8/08 4:42 PM	1	10/8/2008	11/30/2008
SH4-A-L-100808	10/8/08 12:45 PM	10/8/08 4:44 PM	1	10/8/2008	11/30/2008
SH4-A-R-100808	10/8/08 12:45 PM	10/8/08 4:48 PM	1	10/8/2008	11/30/2008
SH5-A-100808	10/8/08 12:46 PM	10/8/08 4:49 PM	1	10/8/2008	11/30/2008
SH6-A-100808	10/8/08 12:47 PM	10/8/08 4:52 PM	1	10/8/2008	11/30/2008
SH7-A-100808	10/8/08 12:48 PM	10/8/08 5:00 PM	1	10/8/2008	11/30/2008
SH8-A-L-100808	10/8/08 12:50 PM	10/8/08 4:59 PM	1	10/8/2008	11/30/2008
SH8-A-R-100808	10/8/08 12:50 PM	10/8/08 4:59 PM	1	10/8/2008	11/30/2008
SH1-B-100908	10/9/08 12:11 PM	10/9/08 12:42 PM	0.9	10/10/2008	11/29/2008
SH2-B-100908	10/9/08 12:18 PM	10/9/08 12:47 PM	0.95	10/10/2008	11/30/2008
SH3-B-100908	10/9/08 12:17 PM	10/9/08 12:49 PM	0.95	10/10/2008	11/30/2008
SH4-B-L-100908	10/9/08 12:16 PM	10/9/08 12:56 PM	1	10/10/2008	11/30/2008
SH4-B-R-100908	10/9/08 12:16 PM	10/9/08 12:56 PM	1	10/10/2008	11/30/2008
SH5-B-100908	10/9/08 12:15 PM	10/9/08 12:58 PM	1	10/10/2008	11/30/2008
SH6-B-100908	10/9/08 12:14 PM	10/9/08 1:01 PM	1	10/10/2008	11/30/2008
SH7-B-100908	10/9/08 12:12 PM	10/9/08 1:03 PM	1	10/10/2008	11/30/2008
SH8-B-L-100908	10/9/08 12:12 PM	10/9/08 1:05 PM	1	10/10/2008	11/30/2008
SH8-B-R-100908	10/9/08 12:12 PM	10/9/08 1:05 PM	1	10/10/2008	11/30/2008
SH1-C-100908	10/9/08 12:45 PM	10/9/08 2:50 PM	0.9	10/10/2008	11/21/2008
SH2-C-100908	10/9/08 12:47 PM	10/9/08 2:53 PM	0.9	10/10/2008	11/21/2008
SH3-C-100908	10/9/08 12:50 PM	10/9/08 2:56 PM	0.9	10/10/2008	11/21/2008
SH4-C-L-100908	10/9/08 12:57 PM	10/9/08 3:01 PM	0.95	10/10/2008	11/21/2008
SH4-C-R-100908	10/9/08 12:57 PM	10/9/08 3:01 PM	0.95	10/10/2008	11/21/2008
SH5-C-100908	10/9/08 12:58 PM	10/9/08 3:05 PM	1	10/10/2008	11/21/2008
SH6-C-100908	10/9/08 1:02 PM	10/9/08 3:08 PM	1	10/10/2008	11/21/2008
SH7-C-100908	10/9/08 1:04 PM	10/9/08 3:09 PM	1	10/10/2008	11/21/2008
SH8-C-L-100908	10/9/08 1:06 PM	10/9/08 3:11 PM	1	10/10/2008	11/21/2008
SH8-C-R-100908	10/9/08 1:06 PM	10/9/08 3:11 PM	1	10/10/2008	11/21/2008
SH1-D-100908	10/9/08 2:51 PM	10/9/08 6:40 PM	0.95	10/10/2008	11/18/2008
SH2-D-100908	10/9/08 2:54 PM	10/9/08 6:43 PM	0.95	10/10/2008	11/18/2008
SH3-D-100908	10/9/08 2:57 PM	10/9/08 6:46 PM	0.9	10/10/2008	11/18/2008
SH4-D-L-100908	10/9/08 3:02 PM	10/9/08 6:50 PM	0.9	10/10/2008	11/18/2008
SH4-D-R-100908	10/9/08 3:02 PM	10/9/08 6:50 PM	0.9	10/10/2008	11/18/2008
SH5-D-100908	10/9/08 3:05 PM	10/9/08 6:54 PM	0.95	10/10/2008	11/18/2008
SH6-D-100908	10/9/08 3:08 PM	10/9/08 6:56 PM	0.95	10/10/2008	11/18/2008
SH7-D-100908	10/9/08 3:09 PM	10/9/08 6:58 PM	1	10/10/2008	11/18/2008
SH8-D-L-100908	10/9/08 3:11 PM	10/9/08 7:00 PM	1	10/10/2008	11/18/2008
SH8-D-R-100908	10/9/08 3:11 PM	10/9/08 7:00 PM	1	10/10/2008	11/18/2008
SH1-E-100908	10/9/08 6:40 PM	10/9/08 10:52 PM	0.85	10/10/2008	11/17/2008
SH2-E-100908	10/9/08 6:44 PM	10/9/08 10:49 PM	1	10/10/2008	11/17/2008

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
SH3-E-100908	10/9/08 6:46 PM	10/9/08 10:47 PM	0.9	10/10/2008	11/17/2008
SH4-E-L-100908	10/9/08 6:52 PM	10/9/08 10:41 PM	0.95	10/10/2008	11/17/2008
SH4-E-R-100908	10/9/08 6:52 PM	10/9/08 10:41 PM	0.95	10/10/2008	11/17/2008
SH5-E-100908	10/9/08 6:55 PM	10/9/08 10:39 PM	0.95	10/10/2008	11/17/2008
SH6-E-100908	10/9/08 6:57 PM	10/9/08 10:37 PM	0.95	10/10/2008	11/17/2008
SH7-E-100908	10/9/08 6:59 PM	10/9/08 10:35 PM	1	10/10/2008	11/17/2008
SH8-E-L-100908	10/9/08 7:01 PM	10/9/08 10:32 PM	1	10/10/2008	11/17/2008
SH8-E-R-100908	10/9/08 7:01 PM	10/9/08 10:32 PM	1	10/10/2008	11/17/2008
SH1-F-100908	10/9/08 10:52 PM	10/10/08 2:40 AM	0.95	10/10/2008	11/16/2008
SH2-F-100908	10/9/08 10:50 PM	10/10/08 2:44 AM	1	10/10/2008	11/16/2008
SH3-F-100908	10/9/08 10:48 PM	10/10/08 2:46 AM	0.95	10/10/2008	11/16/2008
SH4-F-L-100908	10/9/08 10:42 PM	10/10/08 2:52 AM	0.95	10/10/2008	11/16/2008
SH4-F-R-100908	10/9/08 10:42 PM	10/10/08 2:52 AM	0.95	10/10/2008	11/16/2008
SH5-F-100908	10/9/08 10:39 PM	10/10/08 2:55 AM	1	10/10/2008	11/16/2008
SH6-F-100908	10/9/08 10:37 PM	10/10/08 2:57 AM	0.95	10/10/2008	11/16/2008
SH7-F-100908	10/9/08 10:35 PM	10/10/08 3:00 AM	1	10/10/2008	11/16/2008
SH8-F-L-100908	10/9/08 10:33 PM	10/10/08 3:03 AM	1	10/10/2008	11/16/2008
SH8-F-R-100908	10/9/08 10:33 PM	10/10/08 3:03 AM	1	10/10/2008	11/16/2008
SH1-G-101008	10/10/08 2:40 AM	10/10/08 7:14 AM	0.9	10/10/2008	11/15/2008
SH2-G-101008	10/10/08 2:44 AM	10/10/08 7:36 AM	0.9	10/10/2008	11/15/2008
SH3-G-101008	10/10/08 2:46 AM	10/10/08 7:27 AM	0.9	10/10/2008	11/15/2008
SH4-G-L-101008	10/10/08 2:52 AM	10/10/08 7:25 AM	0.85	10/10/2008	11/15/2008
SH4-G-R-101008	10/10/08 2:52 AM	10/10/08 7:25 AM	0.85	10/10/2008	11/15/2008
SH5-G-101008	10/10/08 2:55 AM	10/10/08 7:22 AM	0.95	10/10/2008	11/15/2008
SH6-G-101008	10/10/08 2:57 AM	10/10/08 7:16 AM	0.85	10/10/2008	11/15/2008
SH7-G-101008	10/10/08 3:00 AM	10/10/08 7:44 AM	0.95	10/10/2008	11/15/2008
SH8-G-L-101008	10/10/08 3:03 AM	10/10/08 7:47 AM	0.95	10/10/2008	11/15/2008
SH8-G-R-101008	10/10/08 3:03 AM	10/10/08 7:47 AM	0.95	10/10/2008	11/15/2008
SH1-H-101008	10/10/08 7:14 AM	10/10/08 10:26 AM	0.85	10/13/2008	11/13/2008
SH2-H-101008	10/10/08 7:36 AM	10/10/08 10:32 AM	0.85	10/13/2008	11/13/2008
SH3-H-101008	10/10/08 7:27 AM	10/10/08 10:35 AM	0.85	10/13/2008	11/13/2008
SH4-H-L-101008	10/10/08 7:25 AM	10/10/08 10:43 AM	0.85	10/13/2008	11/13/2008
SH4-H-R-101008	10/10/08 7:25 AM	10/10/08 10:43 AM	0.85	10/13/2008	11/13/2008
SH5-H-101008	10/10/08 7:22 AM	10/10/08 10:57 AM	0.95	10/13/2008	11/13/2008
SH6-H-101008	10/10/08 7:16 AM	10/10/08 10:59 AM	0.95	10/13/2008	11/13/2008
SH7-H-101008	10/10/08 7:44 AM	10/10/08 11:02 AM	0.95	10/13/2008	11/13/2008
SH8-H-L-101008	10/10/08 7:47 AM	10/10/08 11:05 AM	0.95	10/13/2008	11/13/2008
SH8-H-R-101008	10/10/08 7:47 AM	10/10/08 11:05 AM	0.95	10/13/2008	11/13/2008
SH1-I-101008	10/10/08 10:29 AM	10/10/08 2:49 PM	1	10/13/2008	11/12/2008
SH2-I-101008	10/10/08 10:33 AM	10/10/08 2:55 PM	1	10/13/2008	11/12/2008
SH3-I-101008	10/10/08 10:35 AM	10/10/08 2:58 PM	1	10/13/2008	11/12/2008
SH4-I-L-101008	10/10/08 10:43 AM	10/10/08 3:04 PM	1	10/13/2008	11/12/2008
SH4-I-R-101008	10/10/08 10:43 AM	10/10/08 3:04 PM	0.95	10/13/2008	11/12/2008
SH5-I-101008	10/10/08 10:57 AM	10/10/08 3:10 PM	1	10/13/2008	11/12/2008
SH6-I-101008	10/10/08 11:01 AM	10/10/08 3:12 PM	1	10/13/2008	11/12/2008
SH7-I-101008	10/10/08 11:03 AM	10/10/08 3:14 PM	1	10/13/2008	11/12/2008

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
SH8-I-L-101008	10/10/08 11:07 AM	10/10/08 3:16 PM	1	10/13/2008	11/12/2008
SH8-I-R-101008	10/10/08 11:07 AM	10/10/08 3:16 PM	1	10/13/2008	11/12/2008
SH1-J-101008	10/10/08 2:53 PM	10/10/08 6:33 PM	1.05	10/13/2008	11/9/2008
SH2-J-101008	10/10/08 2:55 PM	10/10/08 6:35 PM	1	10/13/2008	11/9/2008
SH3-J-101008	10/10/08 2:58 PM	10/10/08 6:37 PM	1	10/13/2008	11/9/2008
SH4-J-L-101008	10/10/08 3:05 PM	10/10/08 6:43 PM	0.9	10/13/2008	11/9/2008
SH4-J-R-101008	10/10/08 3:05 PM	10/10/08 6:43 PM	0.9	10/13/2008	11/9/2008
SH5-J-101008	10/10/08 3:10 PM	10/10/08 6:45 PM	0.95	10/13/2008	11/9/2008
SH6-J-101008	10/10/08 3:12 PM	10/10/08 6:47 PM	1.05	10/13/2008	11/9/2008
SH7-J-101008	10/10/08 3:14 PM	10/10/08 6:49 PM	1	10/13/2008	11/9/2008
SH8-J-L-101008	10/10/08 3:17 PM	10/10/08 6:51 PM	1	10/13/2008	11/9/2008
SH8-J-R-101008	10/10/08 3:17 PM	10/10/08 6:51 PM	1	10/13/2008	11/9/2008
SH1-K-101008	10/10/08 6:33 PM	10/10/08 10:41 PM	0.95	10/13/2008	11/6/2008
SH2-K-101008	10/10/08 6:35 PM	10/10/08 10:43 PM	0.95	10/13/2008	11/6/2008
SH3-K-101008	10/10/08 6:37 PM	10/10/08 10:46 PM	1	10/13/2008	11/6/2008
SH4-K-L-101008	10/10/08 6:43 PM	10/10/08 10:51 PM	0.9	10/13/2008	11/6/2008
SH4-K-R-101008	10/10/08 6:43 PM	10/10/08 10:51 PM	0.9	10/13/2008	11/6/2008
SH5-K-101008	10/10/08 6:45 PM	10/10/08 10:53 PM	0.95	10/13/2008	11/6/2008
SH6-K-101008	10/10/08 6:47 PM	10/10/08 10:56 PM	1.05	10/13/2008	11/6/2008
SH7-K-101008	10/10/08 6:49 PM	10/10/08 10:58 PM	1	10/13/2008	11/6/2008
SH8-K-L-101008	10/10/08 6:51 PM	10/10/08 11:00 PM	1	10/13/2008	11/6/2008
SH8-K-R-101008	10/10/08 6:51 PM	10/10/08 11:00 PM	1	10/13/2008	11/6/2008
SH1-L-101008	10/10/08 10:41 PM	10/11/08 2:58 AM	0.9	10/13/2008	11/5/2008
SH2-L-101008	10/10/08 10:43 PM	10/11/08 3:00 AM	1	10/13/2008	11/5/2008
SH3-L-101008	10/10/08 10:46 PM	10/11/08 3:02 AM	1	10/13/2008	11/5/2008
SH4-L-L-101008	10/10/08 10:51 PM	10/11/08 3:06 AM	0.9	10/13/2008	11/5/2008
SH4-L-R-101008	10/10/08 10:51 PM	10/11/08 3:06 AM	0.9	10/13/2008	11/5/2008
SH5-L-101008	10/10/08 10:53 PM	10/11/08 3:10 AM	0.95	10/13/2008	11/5/2008
SH6-L-101008	10/10/08 10:56 PM	10/11/08 3:12 AM	1.05	10/13/2008	11/5/2008
SH7-L-101008	10/10/08 10:58 PM	10/11/08 3:13 AM	1	10/13/2008	11/5/2008
SH8-L-L-101008	10/10/08 11:00 PM	10/11/08 3:15 AM	1	10/13/2008	11/5/2008
SH8-L-R-101008	10/10/08 11:00 PM	10/11/08 3:15 AM	1	10/13/2008	11/5/2008
SH1-M-101108	10/11/08 2:58 AM	10/11/08 8:05 AM	0.8	10/13/2008	11/4/2008
SH2-M-101108	10/11/08 3:00 AM	10/11/08 8:08 AM	0.95	10/13/2008	11/4/2008
SH3-M-101108	10/11/08 3:02 AM	10/11/08 8:10 AM	0.95	10/13/2008	11/4/2008
SH4-M-L-101108	10/11/08 3:06 AM	10/11/08 8:23 AM	0.85	10/13/2008	11/4/2008
SH4-M-R-101108	10/11/08 3:06 AM	10/11/08 8:23 AM	0.9	10/13/2008	11/4/2008
SH5-M-101108	10/11/08 3:10 AM	10/11/08 8:24 AM	0.95	10/13/2008	11/4/2008
SH6-M-101108	10/11/08 3:12 AM	10/11/08 8:25 AM	0.95	10/13/2008	11/4/2008
SH7-M-101108	10/11/08 3:13 AM	10/11/08 8:26 AM	0.95	10/13/2008	11/4/2008
SH8-M-L-101108	10/11/08 3:15 AM	10/11/08 8:28 AM	0.95	10/13/2008	11/4/2008
SH8-M-R-101108	10/11/08 3:15 AM	10/11/08 8:28 AM	0.95	10/13/2008	11/4/2008
SH1-N-101108	10/11/08 8:05 AM	10/11/08 11:15 AM	0.9	10/13/2008	11/4/2008
SH2-N-101108	10/11/08 8:08 AM	10/11/08 11:18 AM	0.9	10/13/2008	11/4/2008
SH3-N-101108	10/11/08 8:10 AM	10/11/08 11:19 AM	0.9	10/13/2008	11/4/2008
SH4-N-L-101108	10/11/08 8:23 AM	10/11/08 11:28 AM	0.8	10/13/2008	11/4/2008

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
SH4-N-R-101108	10/11/08 8:23 AM	10/11/08 11:28 AM	0.9	10/13/2008	11/4/2008
SH5-N-101108	10/11/08 8:24 AM	10/11/08 11:31 AM	0.9	10/13/2008	11/4/2008
SH6-N-101108	10/11/08 8:25 AM	10/11/08 11:34 AM	0.95	10/13/2008	11/4/2008
SH7-N-101108	10/11/08 8:26 AM	10/11/08 11:37 AM	0.9	10/13/2008	11/4/2008
SH8-N-L-101108	10/11/08 8:28 AM	10/11/08 11:41 AM	0.9	10/13/2008	11/4/2008
SH8-N-R-101108	10/11/08 8:28 AM	10/11/08 11:41 AM	0.9	10/13/2008	11/4/2008
SH1-O-101108	10/11/08 11:15 AM	10/11/08 3:17 PM	0.8	10/13/2008	10/28/2008
SH2-O-101108	10/11/08 11:18 AM	10/11/08 3:18 PM	0.9	10/13/2008	10/28/2008
SH3-O-101108	10/11/08 11:19 AM	10/11/08 3:20 PM	0.9	10/13/2008	10/28/2008
SH4-O-L-101108	10/11/08 11:28 AM	10/11/08 3:28 PM	0.8	10/13/2008	10/28/2008
SH4-O-R-101108	10/11/08 11:28 AM	10/11/08 3:28 PM	0.9	10/13/2008	10/28/2008
SH5-O-101108	10/11/08 11:31 AM	10/11/08 3:30 PM	0.9	10/13/2008	10/28/2008
SH6-O-101108	10/11/08 11:34 AM	10/11/08 3:31 PM	1	10/13/2008	10/28/2008
SH7-O-101108	10/11/08 11:37 AM	10/11/08 3:33 PM	0.9	10/13/2008	10/28/2008
SH8-O-L-101108	10/11/08 11:41 AM	10/11/08 3:34 PM	0.9	10/13/2008	10/28/2008
SH8-O-R-101108	10/11/08 11:41 AM	10/11/08 3:34 PM	0.9	10/13/2008	10/28/2008
SH1-P-101108	10/11/08 3:17 PM	10/11/08 11:05 PM	0.85	10/13/2008	10/30/2008
SH2-P-101108	10/11/08 3:18 PM	10/11/08 11:07 PM	0.9	10/13/2008	10/30/2008
SH3-P-101108	10/11/08 3:20 PM	10/11/08 11:08 PM	0.9	10/13/2008	10/30/2008
SH4-P-L-101108	10/11/08 3:28 PM	10/11/08 11:20 PM	0.85	10/13/2008	10/30/2008
SH4-P-R-101108	10/11/08 3:28 PM	10/11/08 11:20 PM	0.85	10/13/2008	10/30/2008
SH5-P-101108	10/11/08 3:30 PM	10/11/08 11:23 PM	0.9	10/13/2008	10/30/2008
SH6-P-101108	10/11/08 3:31 PM	10/11/08 11:24 PM	1	10/13/2008	10/30/2008
SH7-P-101108	10/11/08 3:33 PM	10/11/08 11:26 PM	1	10/13/2008	10/30/2008
SH8-P-L-101108	10/11/08 3:34 PM	10/11/08 11:28 PM	0.9	10/13/2008	10/30/2008
SH8-P-R-101108	10/11/08 3:34 PM	10/11/08 11:28 PM	0.9	10/13/2008	10/30/2008
SH1-Q-101108	10/11/08 11:05 PM	10/12/08 7:26 AM	0.85	10/13/2008	10/27/2008
SH2-Q-101108	10/11/08 11:07 PM	10/12/08 7:27 AM	0.9	10/13/2008	10/27/2008
SH3-Q-101108	10/11/08 11:08 PM	10/12/08 7:29 AM	0.85	10/13/2008	10/27/2008
SH4-Q-L-101108	10/11/08 11:20 PM	10/12/08 7:38 AM	0.75	10/13/2008	10/27/2008
SH4-Q-R-101108	10/11/08 11:20 PM	10/12/08 7:38 AM	0.75	10/13/2008	10/27/2008
SH5-Q-101108	10/11/08 11:23 PM	10/12/08 7:43 AM	0.9	10/13/2008	10/27/2008
SH6-Q-101108	10/11/08 11:24 PM	10/12/08 7:44 AM	0.95	10/13/2008	10/27/2008
SH7-Q-101108	10/11/08 11:26 PM	10/12/08 7:46 AM	1	10/13/2008	10/27/2008
SH8-Q-L-101108	10/11/08 11:28 PM	10/12/08 7:48 AM	0.85	10/13/2008	10/27/2008
SH8-Q-R-101108	10/11/08 11:28 PM	10/12/08 7:48 AM	0.85	10/13/2008	10/27/2008
SH1-R-101208	10/12/08 7:26 AM	10/12/08 2:51 PM	0.85	10/13/2008	10/26/2008
SH2-R-101208	10/12/08 7:27 AM	10/12/08 2:53 PM	0.95	10/13/2008	10/26/2008
SH3-R-101208	10/12/08 7:29 AM	10/12/08 2:55 PM	0.95	10/13/2008	10/26/2008
SH4-R-L-101208	10/12/08 7:38 AM	10/12/08 3:14 PM	0.85	10/13/2008	10/26/2008
SH4-R-R-101208	10/12/08 7:38 AM	10/12/08 3:14 PM	0.85	10/13/2008	10/26/2008
SH5-R-101208	10/12/08 7:43 AM	10/12/08 3:15 PM	0.9	10/13/2008	10/26/2008
SH6-R-101208	10/12/08 7:44 AM	10/12/08 3:18 PM	1	10/13/2008	10/26/2008
SH7-R-101208	10/12/08 7:46 AM	10/12/08 3:20 PM	1	10/13/2008	10/26/2008
SH8-R-L-101208	10/12/08 7:48 AM	10/12/08 3:22 PM	0.95	10/13/2008	10/26/2008
SH8-R-R-101208	10/12/08 7:48 AM	10/12/08 3:22 PM	0.95	10/13/2008	10/26/2008

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
SH1-S-101208	10/12/08 2:51 PM	10/12/08 10:58 PM	0.9	10/13/2008	10/22/2008
SH2-S-101208	10/12/08 2:53 PM	10/12/08 11:00 PM	0.95	10/13/2008	10/22/2008
SH3-S-101208	10/12/08 2:55 PM	10/12/08 11:02 PM	1	10/13/2008	10/22/2008
SH4-S-L-101208	10/12/08 3:14 PM	10/12/08 11:06 PM	0.9	10/13/2008	10/22/2008
SH4-S-R-101208	10/12/08 3:14 PM	10/12/08 11:06 PM	0.9	10/13/2008	10/22/2008
SH5-S-101208	10/12/08 3:15 PM	10/12/08 11:08 PM	0.95	10/13/2008	10/22/2008
SH6-S-101208	10/12/08 3:18 PM	10/12/08 11:10 PM	1.05	10/13/2008	10/22/2008
SH7-S-101208	10/12/08 3:20 PM	10/12/08 11:13 PM	1	10/13/2008	10/22/2008
SH8-S-L-101208	10/12/08 3:22 PM	10/12/08 11:15 PM	0.95	10/13/2008	10/22/2008
SH8-S-R-101208	10/12/08 3:22 PM	10/12/08 11:15 PM	0.95	10/13/2008	10/22/2008
SH1-T-101208	10/12/08 10:58 PM	10/13/08 7:43 AM	0.85	10/13/2008	10/20/2008
SH2-T-101208	10/12/08 11:00 PM	10/13/08 7:45 AM	0.95	10/13/2008	10/20/2008
SH3-T-101208	10/12/08 11:02 PM	10/13/08 7:25 AM	1	10/13/2008	10/20/2008
SH4-T-L-101208	10/12/08 11:06 PM	10/13/08 7:28 AM	0.9	10/13/2008	10/20/2008
SH4-T-R-101208	10/12/08 11:06 PM	10/13/08 7:28 AM	0.9	10/13/2008	10/20/2008
SH5-T-101208	10/12/08 11:08 PM	10/13/08 7:30 AM	1	10/13/2008	10/20/2008
SH6-T-101208	10/12/08 11:10 PM	10/13/08 7:32 AM	1	10/13/2008	10/20/2008
SH7-T-101208	10/12/08 11:13 PM	10/13/08 7:34 AM	1	10/13/2008	10/20/2008
SH8-T-L-101208	10/12/08 11:15 PM	10/13/08 7:38 AM	0.9	10/13/2008	10/20/2008
SH8-T-R-101208	10/12/08 11:15 PM	10/13/08 7:38 AM	0.95	10/13/2008	10/20/2008
SH1-U-101308	10/13/08 7:43 AM	10/13/08 11:40 AM	0.8	10/13/2008	10/19/2008
SH2-U-101308	10/13/08 7:45 AM	10/13/08 11:41 AM	1	10/13/2008	10/19/2008
SH3-U-101308	10/13/08 7:25 AM	10/13/08 11:35 AM	1	10/13/2008	10/19/2008
SH4-U-L-101308	10/13/08 7:28 AM	10/13/08 11:36 AM	0.9	10/13/2008	10/19/2008
SH4-U-R-101308	10/13/08 7:28 AM	10/13/08 11:36 AM	0.9	10/13/2008	10/19/2008
SH5-U-101308	10/13/08 7:30 AM	10/13/08 11:36 AM	1	10/13/2008	10/19/2008
SH6-U-101308	10/13/08 7:32 AM	10/13/08 11:37 AM	0.95	10/13/2008	10/19/2008
SH7-U-101308	10/13/08 7:34 AM	10/13/08 11:38 AM	1	10/13/2008	10/19/2008
SH8-U-L-101308	10/13/08 7:38 AM	10/13/08 11:39 AM	0.95	10/13/2008	10/19/2008
SH8-U-R-101308	10/13/08 7:38 AM	10/13/08 11:39 AM	1	10/13/2008	10/19/2008

**Table 12**  
**Near Field Additional Air Samples**

<b>Sample ID</b>	<b>Air sampler start time</b>	<b>Air sampler end time</b>	<b>Average flow rate (L/min)</b>	<b>Date transferred to -80°C</b>	<b>Date of extraction</b>
W-A-100808	10/8/08 12:41 PM	10/8/08 4:40 PM	1	10/8/2008	11/30/2008
X-A-100808	10/8/08 12:43 PM	10/8/08 4:44 PM	1	10/8/2008	11/30/2008
Y-A-100808	10/8/08 12:47 PM	10/8/08 4:48 PM	1	10/8/2008	11/30/2008
Z-A-100808	10/8/08 12:55 PM	10/8/08 5:03 PM	1	10/8/2008	11/30/2008
W-B-100908	10/9/08 11:36 AM	10/9/08 12:53 PM	1	10/10/2008	11/30/2008
X-B-100908	10/9/08 11:34 AM	10/9/08 1:48 PM	1	10/10/2008	11/30/2008
Y-B-100908	10/9/08 11:33 AM	10/9/08 1:44 PM	1	10/10/2008	11/30/2008
Z-B-100908	10/9/08 11:40 AM	10/9/08 1:09 PM	1	10/10/2008	11/30/2008
W-C-100908	10/9/08 12:54 PM	10/9/08 2:58 PM	1	10/10/2008	11/21/2008
X-C-100908	10/9/08 1:40 PM	10/9/08 3:18 PM	1	10/10/2008	11/28/2008
Y-C-100908	10/9/08 1:45 PM	10/9/08 3:22 PM	0.9	10/10/2008	11/28/2008
Z-C-100908	10/9/08 1:10 PM	10/9/08 3:15 PM	1	10/10/2008	11/21/2008
W-D-100908	10/9/08 2:58 PM	10/9/08 6:48 PM	1.05	10/10/2008	11/18/2008
X-D-100908	10/9/08 3:18 PM	10/9/08 7:12 PM	1	10/10/2008	11/21/2008
Y-D-100908	10/9/08 3:22 PM	10/9/08 7:15 PM	0.9	10/10/2008	11/21/2008
Z-D-100908	10/9/08 3:15 PM	10/9/08 7:05 PM	1	10/10/2008	11/18/2008
W-E-100908	10/9/08 6:49 PM	10/9/08 10:44 PM	1.05	10/10/2008	11/17/2008
X-E-100908	10/9/08 7:12 PM	10/9/08 11:00 PM	1	10/10/2008	11/18/2008
Y-E-100908	10/9/08 7:15 PM	10/9/08 10:55 PM	0.9	10/10/2008	11/18/2008
Z-E-100908	10/9/08 7:06 PM	10/9/08 10:57 PM	1	10/10/2008	11/17/2008
W-F-100908	10/9/08 10:45 PM	10/10/08 2:50 AM	1	10/10/2008	11/16/2008
X-F-100908	10/9/08 11:00 PM	10/10/08 3:10 AM	1	10/10/2008	11/17/2008
Y-F-100908	10/9/08 10:55 PM	10/10/08 3:07 AM	0.9	10/10/2008	11/17/2008
Z-F-100908	10/9/08 10:57 PM	10/10/08 3:08 AM	1	10/10/2008	11/16/2008
W-G-101008	10/10/08 2:50 AM	10/10/08 7:32 AM	0.95	10/10/2008	11/15/2008
X-G-101008	10/10/08 3:10 AM	10/10/08 7:38 AM	1.05	10/10/2008	11/16/2008
Y-G-101008	10/10/08 3:07 AM	10/10/08 7:33 AM	0.95	10/10/2008	11/16/2008
Z-G-101008	10/10/08 3:08 AM	10/10/08 7:50 AM	0.95	10/10/2008	11/15/2008
W-H-101008	10/10/08 7:32 AM	10/10/08 10:39 AM	1.0	10/13/2008	11/13/2008
X-H-101008	10/10/08 7:38 AM	10/10/08 11:19 AM	1.2	10/13/2008	11/13/2008
Y-H-101008	10/10/08 7:33 AM	10/10/08 11:14 AM	1.0	10/13/2008	11/13/2008
Z-H-101008	10/10/08 7:50 AM	10/10/08 10:21 AM	1.0	10/13/2008	11/13/2008
W-I-101008	10/10/08 10:41 AM	10/10/08 3:02 PM	1.1	10/13/2008	11/12/2008
X-I-101008	10/10/08 11:19 AM	10/10/08 3:39 PM	1.1	10/13/2008	11/13/2008
Y-I-101008	10/10/08 11:14 AM	10/10/08 3:33 PM	1.0	10/13/2008	11/13/2008
Z-I-101008	10/10/08 10:21 AM	10/10/08 3:27 PM	1.0	10/13/2008	11/12/2008
W-J-101008	10/10/08 3:02 PM	10/10/08 6:40 PM	1.1	10/13/2008	11/9/2008
X-J-101008	10/10/08 3:39 PM	10/10/08 7:02 PM	1.1	10/13/2008	11/12/2008
Y-J-101008	10/10/08 3:33 PM	10/10/08 6:58 PM	1.0	10/13/2008	11/12/2008
Z-J-101008	10/10/08 3:27 PM	10/10/08 6:55 PM	1.0	10/13/2008	11/9/2008
W-K-101008	10/10/08 6:40 PM	10/10/08 10:48 PM	1.0	10/13/2008	11/6/2008
X-K-101008	10/10/08 7:02 PM	10/10/08 11:10 PM	1.0	10/13/2008	11/9/2008

Sample ID	Air sampler start time	Air sampler end time	Average flow rate (L/min)	Date transferred to -80°C	Date of extraction
Y-K-101008	10/10/08 6:58 PM	10/10/08 11:05 PM	0.9	10/13/2008	11/9/2008
Z-K-101008	10/10/08 6:55 PM	10/10/08 11:03 PM	1.0	10/13/2008	11/6/2008
W-L-101008	10/10/08 10:48 PM	10/11/08 3:04 AM	1.0	10/13/2008	11/5/2008
X-L-101008	10/10/08 11:10 PM	10/11/08 3:24 AM	1.0	10/13/2008	11/6/2008
Y-L-101008	10/10/08 11:05 PM	10/11/08 3:22 AM	0.9	10/13/2008	11/6/2008
Z-L-101008	10/10/08 11:03 PM	10/11/08 3:19 AM	1.0	10/13/2008	11/5/2008
W-M-101108 <sup>a</sup>	10/11/08 3:04 AM	10/11/08 8:15 AM	Failed	10/13/2008	11/4/2008
X-M-101108	10/11/08 3:24 AM	10/11/08 8:00 AM	1.00	10/13/2008	11/4/2008
Y-M-101108	10/11/08 3:22 AM	10/11/08 7:55 AM	0.85	10/13/2008	11/4/2008
Z-M-101108	10/11/08 3:19 AM	10/11/08 8:35 AM	1.00	10/13/2008	11/4/2008
W-N-101108	10/11/08 8:15 AM	10/11/08 11:23 AM	0.95	10/13/2008	11/4/2008
X-N-101108	10/11/08 8:00 AM	10/11/08 10:35 AM	1.00	10/13/2008	11/5/2008
Y-N-101108	10/11/08 7:55 AM	10/11/08 11:05 AM	0.90	10/13/2008	11/5/2008
Z-N-101108	10/11/08 8:35 AM	10/11/08 11:45 AM	1.00	10/13/2008	11/4/2008
W-O-101108	10/11/08 11:23 AM	10/11/08 3:25 PM	1.00	10/13/2008	10/28/2008
X-O-101108	10/11/08 10:35 AM	10/11/08 2:40 PM	1.00	10/13/2008	10/30/2008
Y-O-101108	10/11/08 11:05 AM	10/11/08 3:10 PM	0.90	10/13/2008	10/30/2008
Z-O-101108	10/11/08 11:45 AM	10/11/08 3:37 PM	1.00	10/13/2008	10/28/2008
W-P-101108 <sup>a</sup>	10/11/08 3:25 PM	10/11/08 11:14 PM	Failed	10/13/2008	10/30/2008
X-P-101108	10/11/08 3:10 PM	10/11/08 11:00 PM	1.00	10/13/2008	11/3/2008
Y-P-101108	10/11/08 2:40 PM	10/11/08 10:40 PM	0.90	10/13/2008	11/3/2008
Z-P-101108	10/11/08 3:37 PM	10/11/08 11:32 PM	1.00	10/13/2008	10/30/2008
W-Q-101108 <sup>a</sup>	10/11/08 11:14 PM	10/12/08 7:32 AM	Failed	10/13/2008	10/27/2008
X-Q-101108	10/11/08 11:00 PM	10/12/08 7:17 AM	0.95	10/13/2008	10/27/2008
Y-Q-101108	10/11/08 10:40 PM	10/12/08 6:48 AM	0.90	10/13/2008	10/27/2008
Z-Q-101108	10/11/08 11:32 PM	10/12/08 7:54 AM	0.95	10/13/2008	10/27/2008
W-R-101208	10/12/08 7:32 AM	10/12/08 2:58 PM	1.0	10/13/2008	10/26/2008
X-R-101208	10/12/08 7:17 AM	10/12/08 3:32 PM	1.0	10/13/2008	10/26/2008
Y-R-101208	10/12/08 6:48 AM	10/12/08 3:35 PM	1.0	10/13/2008	10/26/2008
Z-R-101208	10/12/08 7:54 AM	10/12/08 3:25 PM	1.0	10/13/2008	10/26/2008
W-S-101208	10/12/08 2:58 PM	10/12/08 11:04 PM	1.1	10/13/2008	10/22/2008
X-S-101208	10/12/08 3:35 PM	10/12/08 10:31 PM	1.0	10/13/2008	10/23/2008
Y-S-101208	10/12/08 3:32 PM	10/12/08 10:30 PM	1.0	10/13/2008	10/23/2008
Z-S-101208	10/12/08 3:25 PM	10/12/08 11:17 PM	1.0	10/13/2008	10/22/2008
W-T-101208 <sup>a</sup>	10/12/08 11:04 PM	10/12/08 11:43 PM	Failed	10/13/2008	10/20/2008
X-T-101208	10/12/08 10:31 PM	10/13/08 7:13 AM	1.05	10/13/2008	10/21/2008
Y-T-101208	10/12/08 10:30 PM	10/13/08 7:15 AM	1.00	10/13/2008	10/21/2008
Z-T-101208	10/12/08 11:17 PM	10/13/08 7:48 AM	1.00	10/13/2008	10/20/2008
W-U-101308	10/13/08 7:19 AM	10/13/08 11:34 AM	1.00	10/13/2008	10/20/2008
X-U-101308	10/13/08 7:15 AM	10/13/08 12:16 PM	1.10	10/13/2008	10/20/2008
Y-U-101308	10/13/08 7:13 AM	10/13/08 12:14 PM	1.00	10/13/2008	10/20/2008
Z-U-101308	10/13/08 7:48 AM	10/13/08 11:43 AM	1.00	10/13/2008	10/20/2008

<sup>a</sup> The air sample pump failed on these samples.

**APPENDIX D: 1 Hour Averaged Weather Data, October 7-13th, 2008 (HOBO Weather Station)**

Date	Time (PST)	Avg: Air Temp, °C	Avg: Wind Speed, m/s	Avg: Gust Speed, m/s	Avg: Wind Direction ø	Avg: Soil Temp, °C	Avg: Water Content, m <sup>3</sup> /m <sup>3</sup>	Avg: Rain, mm
10/7/2008	11:00	17.698	6.96	8.93	62.5	14.661	0.142	0
10/7/2008	12:00	18.21	7.16	9.06	63.2	14.811	0.144	0
10/7/2008	13:00	18.484	7.16	8.99	70.5	15.146	0.145	0
10/7/2008	14:00	18.871	6.91	8.66	68.3	15.574	0.146	0
10/7/2008	15:00	18.482	7.54	9.45	58.1	15.983	0.147	0
10/7/2008	16:00	18.086	6.24	7.77	68.4	16.193	0.147	0
10/7/2008	17:00	16.417	5.13	6.19	101.6	16.237	0.146	0
10/7/2008	18:00	12.609	2.1	2.56	160.1	16.017	0.145	0
10/7/2008	19:00	11.028	3	3.57	120.1	15.488	0.143	0
10/7/2008	20:00	10.016	2.77	3.29	101.2	14.853	0.141	0
10/7/2008	21:00	9.215	2.58	3.16	74.7	14.244	0.14	0
10/7/2008	22:00	8.149	1.98	2.36	91.5	13.706	0.139	0
10/7/2008	23:00	7.445	2.23	2.58	75.7	13.227	0.138	0

Date	Time (PST)	Avg: Air Temp, °C	Avg: Wind Speed, m/s	Avg: Gust Speed, m/s	Avg: Wind Direction ø	Avg: Soil Temp, °C	Avg: Water Content, m <sup>3</sup> /m <sup>3</sup>	Avg: Rain, mm
10/8/2008	0:00	5.163	0.87	1.17	139.9	12.758	0.137	0
10/8/2008	1:00	5.708	1.79	2.08	96.5	12.263	0.135	0
10/8/2008	2:00	3.579	0.97	1.2	156.6	11.811	0.134	0
10/8/2008	3:00	3.18	0.87	1.1	180.2	11.375	0.133	0
10/8/2008	4:00	1.724	1.18	1.4	134	10.934	0.133	0
10/8/2008	5:00	1.216	0.69	0.96	127.1	10.511	0.132	0
10/8/2008	6:00	3.619	2.22	2.54	35.8	10.117	0.131	0
10/8/2008	7:00	3.523	1.64	1.93	164.9	9.811	0.131	0
10/8/2008	8:00	5.604	0.87	1.1	282.9	9.623	0.13	0
10/8/2008	9:00	10.314	1.49	2.03	102.9	9.695	0.131	0
10/8/2008	10:00	12.049	1.88	2.54	76.5	10.16	0.133	0
10/8/2008	11:00	13.444	1.29	1.99	145.6	10.965	0.136	0
10/8/2008	12:00	14.279	1.47	2.21	167.7	12.042	0.138	0
10/8/2008	13:00	14.931	2.3	3.17	219	13.23	0.141	0
10/8/2008	14:00	15.001	2.48	3.32	194.9	14.302	0.142	0
10/8/2008	15:00	15.31	1.9	2.66	189.5	15.086	0.142	0
10/8/2008	16:00	14.997	1.67	2.17	289.8	15.569	0.141	0
10/8/2008	17:00	13.738	1.55	1.84	302.3	15.698	0.139	0
10/8/2008	18:00	10.749	0.46	0.55	299.7	15.408	0.136	0
10/8/2008	19:00	7.851	0.62	0.75	151.9	14.737	0.133	0
10/8/2008	20:00	5.971	0.04	0.06	102.5	13.937	0.13	0
10/8/2008	21:00	5.269	0.6	0.72	113.9	13.178	0.129	0
10/8/2008	22:00	3.978	1.17	1.34	123.4	12.502	0.128	0
10/8/2008	23:00	2.864	1.52	1.75	121.2	11.912	0.127	0

Date	Time (PST)	Avg: Air Temp, °C	Avg: Wind Speed, m/s	Avg: Gust Speed, m/s	Avg: Wind Direction ø	Avg: Soil Temp, °C	Avg: Water Content, m <sup>3</sup> /m <sup>3</sup>	Avg: Rain, mm
10/9/2008	0:00	4.713	1.11	1.5	250.5	11.41	0.127	0
10/9/2008	1:00	3.396	0.44	0.62	183.3	10.987	0.126	0
10/9/2008	2:00	1.816	0.63	0.82	157.1	10.583	0.126	0
10/9/2008	3:00	0.93	0.14	0.21	222.5	10.171	0.125	0
10/9/2008	4:00	0.789	0.35	0.43	204.4	9.754	0.125	0
10/9/2008	5:00	0.47	0.26	0.33	35.8	9.36	0.124	0
10/9/2008	6:00	0.715	0.45	0.64	202.6	9.023	0.123	0
10/9/2008	7:00	0.78	0.4	0.54	129.6	8.713	0.123	0
10/9/2008	8:00	4.115	0.58	0.77	199.1	8.478	0.122	0
10/9/2008	9:00	6.002	1.29	1.7	281.8	8.536	0.123	0
10/9/2008	10:00	8.674	0.99	1.49	195.2	9.034	0.125	0
10/9/2008	11:00	10.752	2.23	3.09	110.4	9.914	0.128	0
10/9/2008	12:00	11.679	2.97	3.91	117.1	10.904	0.13	0
10/9/2008	13:00	12.729	3.62	4.75	106.6	11.759	0.131	0
10/9/2008	14:00	13.253	3.14	4.2	101.9	12.499	0.132	0
10/9/2008	15:00	13.171	2.68	3.54	82.1	13.102	0.132	0
10/9/2008	16:00	12.471	1.42	1.77	101.9	13.376	0.131	0
10/9/2008	17:00	10.888	1.54	1.83	36.5	13.337	0.129	0
10/9/2008	18:00	8.698	1.65	1.87	47.3	13.072	0.128	0
10/9/2008	19:00	7.561	2.17	2.55	58.9	12.658	0.125	0
10/9/2008	20:00	5.751	1.53	1.73	61.7	12.181	0.124	0
10/9/2008	21:00	5.236	1.06	1.29	148.4	11.704	0.123	0
10/9/2008	22:00	5.125	0.69	0.89	164.8	11.268	0.122	0
10/9/2008	23:00	4.871	0.76	0.96	110.6	10.923	0.122	0

Date	Time (PST)	Avg: Air Temp, °C	Avg: Wind Speed, m/s	Avg: Gust Speed, m/s	Avg: Wind Direction ø	Avg: Soil Temp, °C	Avg: Water Content, m <sup>3</sup> /m <sup>3</sup>	Avg: Rain, mm
10/10/2008	0:00	4.562	0.76	0.91	197.5	10.645	0.122	0
10/10/2008	1:00	3.377	0.46	0.64	129.1	10.365	0.122	0
10/10/2008	2:00	2.191	1.27	1.48	114.7	10.014	0.121	0
10/10/2008	3:00	1.326	1.33	1.53	124.2	9.667	0.12	0
10/10/2008	4:00	2.904	2.89	3.51	159.5	9.33	0.119	0
10/10/2008	5:00	2.168	4.24	5.19	175.5	9.034	0.119	0
10/10/2008	6:00	1.121	3.40	4.07	172.8	8.767	0.118	0
10/10/2008	7:00	1.44	3.06	3.7	172.4	8.486	0.118	0
10/10/2008	8:00	2.796	3.33	3.97	165.2	8.247	0.117	0
10/10/2008	9:00	5.746	2.48	3.14	169.1	8.164	0.118	0
10/10/2008	10:00	9.499	3.23	4.05	183.1	8.432	0.119	0
10/10/2008	11:00	13.105	4.5	5.75	202.7	9.099	0.121	0
10/10/2008	12:00	14.35	5.82	7.1	212.1	10.014	0.123	0
10/10/2008	13:00	14.844	6.34	7.84	204.5	10.954	0.124	0
10/10/2008	14:00	15.142	6.39	7.82	199.3	11.78	0.125	0
10/10/2008	15:00	15.037	6.71	8.25	199.3	12.414	0.125	0

Date	Time (PST)	Avg: Air Temp, °C	Avg: Wind Speed, m/s	Avg: Gust Speed, m/s	Avg: Wind Direction ø	Avg: Soil Temp, °C	Avg: Water Content, m <sup>3</sup> /m <sup>3</sup>	Avg: Rain, mm
10/10/2008	16:00	14.402	7.02	8.51	196	12.777	0.124	0
10/10/2008	17:00	12.878	5.88	7.16	193.2	12.826	0.123	0
10/10/2008	18:00	10.483	4.71	5.67	196.8	12.606	0.121	0
10/10/2008	19:00	9.268	4.9	5.91	194.2	12.168	0.119	0
10/10/2008	20:00	8.07	4.91	5.95	197.9	11.68	0.118	0
10/10/2008	21:00	6.76	4.61	5.62	194.8	11.215	0.117	0
10/10/2008	22:00	7.287	4.94	6	203	10.787	0.116	0
10/10/2008	23:00	6.68	5.19	6.3	205.8	10.463	0.116	0

Date	Time (PST)	Avg: Air Temp, °C	Avg: Wind Speed, m/s	Avg: Gust Speed, m/s	Avg: Wind Direction ø	Avg: Soil Temp, °C	Avg: Water Content, m <sup>3</sup> /m <sup>3</sup>	Avg: Rain, mm
10/11/2008	0:00	5.261	4.66	5.61	211	10.173	0.116	0
10/11/2008	1:00	5.127	4.54	5.51	212	9.829	0.115	0
10/11/2008	2:00	3.889	4.03	4.82	198.4	9.486	0.114	0
10/11/2008	3:00	3.366	4.8	5.76	195.4	9.15	0.114	0
10/11/2008	4:00	3.127	4.78	5.79	187.1	8.823	0.113	0
10/11/2008	5:00	1.597	2.58	3.09	177	8.527	0.113	0
10/11/2008	6:00	-0.153	2.7	3.14	152.9	8.191	0.112	0
10/11/2008	7:00	1.208	4.95	5.82	163.9	7.826	0.111	0
10/11/2008	8:00	2.993	5.03	6.07	166.6	7.563	0.111	0
10/11/2008	9:00	5.805	5.56	6.72	169.9	7.507	0.111	0
10/11/2008	10:00	8.907	6.12	7.29	163.3	7.748	0.113	0
10/11/2008	11:00	12.262	6.7	8.13	179.1	8.319	0.115	0
10/11/2008	12:00	13.519	7.08	8.6	186.2	9.125	0.116	0
10/11/2008	13:00	13.956	8.16	9.95	187.1	10.007	0.118	0
10/11/2008	14:00	14.324	7.96	9.65	188.7	10.778	0.119	0
10/11/2008	15:00	14.514	7.17	8.73	177.4	11.399	0.119	0
10/11/2008	16:00	14.19	6.41	7.7	176	11.837	0.118	0
10/11/2008	17:00	12.393	3.65	4.36	167	12.024	0.117	0
10/11/2008	18:00	7.609	1.72	1.96	167.4	11.894	0.115	0
10/11/2008	19:00	6.229	1.95	2.12	163.7	11.419	0.113	0
10/11/2008	20:00	4.736	1.8	2.06	153.8	10.824	0.111	0
10/11/2008	21:00	3.707	1.36	1.63	142.2	10.241	0.11	0
10/11/2008	22:00	4.828	2.84	3.21	173.3	9.717	0.109	0
10/11/2008	23:00	4.334	3.14	3.53	170.4	9.297	0.109	0

Date	Time (PST)	Avg: Air Temp, °C	Avg: Wind Speed, m/s	Avg: Gust Speed, m/s	Avg: Wind Direction ø	Avg: Soil Temp, °C	Avg: Water Content, m <sup>3</sup> /m <sup>3</sup>	Avg: Rain, mm
10/12/2008	0:00	3.019	2.12	2.53	193.1	8.962	0.109	0
10/12/2008	1:00	0.503	0.8	1.05	91.7	8.63	0.108	0
10/12/2008	2:00	0.566	0.83	1.03	190.7	8.239	0.108	0

Date	Time (PST)	Avg: Air Temp, °C	Avg: Wind Speed, m/s	Avg: Gust Speed, m/s	Avg: Wind Direction ø	Avg: Soil Temp, °C	Avg: Water Content, m <sup>3</sup> /m <sup>3</sup>	Avg: Rain, mm
10/12/2008	3:00	0.486	0.57	0.82	172.1	7.827	0.107	0
10/12/2008	4:00	-0.307	0.71	0.89	191.6	7.443	0.106	0
10/12/2008	5:00	-1.464	1.39	1.63	128.7	7.076	0.106	0
10/12/2008	6:00	-1.025	1.46	1.74	224.7	6.741	0.105	0
10/12/2008	7:00	-1.073	1.54	1.92	198.6	6.455	0.102	0
10/12/2008	8:00	0.438	1.46	1.77	268.7	6.235	0.1	0
10/12/2008	9:00	3.464	2.01	2.49	283.8	6.234	0.101	0
10/12/2008	10:00	6.442	2.26	2.93	318	6.607	0.101	0
10/12/2008	11:00	9.373	1.94	2.7	229.4	7.368	0.102	0
10/12/2008	12:00	11.42	1.84	2.6	185.2	8.449	0.105	0
10/12/2008	13:00	12.825	2.04	2.99	109.2	9.67	0.107	0
10/12/2008	14:00	14.443	1.51	2.34	65.8	10.827	0.108	0
10/12/2008	15:00	14.655	1.86	2.6	63.4	11.809	0.109	0
10/12/2008	16:00	14.074	2.39	2.89	173.2	12.441	0.109	0
10/12/2008	17:00	12.032	1.74	2.05	27.1	12.554	0.107	0
10/12/2008	18:00	8.652	1.21	1.35	68.2	12.284	0.104	0
10/12/2008	19:00	6.356	1.17	1.34	240.9	11.762	0.102	0
10/12/2008	20:00	5.71	0.73	0.92	277.9	11.173	0.1	0
10/12/2008	21:00	4.917	0.37	0.5	235.5	10.626	0.098	0
10/12/2008	22:00	5.106	0.31	0.4	222.9	10.119	0.097	0
10/12/2008	23:00	5.217	0.28	0.36	249.6	9.664	0.096	0

Date	Time (PST)	Avg: Air Temp, °C	Avg: Wind Speed, m/s	Avg: Gust Speed, m/s	Avg: Wind Direction ø	Avg: Soil Temp, °C	Avg: Water Content, m <sup>3</sup> /m <sup>3</sup>	Avg: Rain, mm
10/13/2008	0:00	4.272	0.49	0.61	257.5	9.266	0.096	0
10/13/2008	1:00	3.95	0.46	0.6	254.7	8.912	0.096	0
10/13/2008	2:00	3.799	0.45	0.62	187	8.602	0.096	0
10/13/2008	3:00	3.336	0.53	0.65	251.2	8.32	0.095	0
10/13/2008	4:00	3.105	0.8	0.98	258.7	8.064	0.095	0
10/13/2008	5:00	2.489	0.56	0.7	252.6	7.84	0.095	0
10/13/2008	6:00	3.081	0.82	0.94	268.7	7.651	0.094	0
10/13/2008	7:00	3.847	0.72	0.92	266.4	7.5	0.094	0
10/13/2008	8:00	6.295	0.92	1.15	262.9	7.461	0.094	0
10/13/2008	9:00	10.803	1.99	2.48	285.1	7.676	0.095	0
10/13/2008	10:00	13.177	3.61	4.44	201.7	8.236	0.097	0
10/13/2008	11:00	15.516	4.38	5.35	90	9.061	0.1	0
10/13/2008	12:00	17.1	4.58	5.73	45.2	9.876	0.101	0
10/13/2008	13:00	17.1	4.58	5.73	45.2	9.876	0.101	0

## APPENDIX E: WORKING METHOD

Food and Environmental Quality Laboratory  
Washington State University

FEQL Project Number: 1008

### WORKING ANALYTICAL METHOD DETERMINATION OF RESIDUES OF MITC IN CHARCOAL AIR SAMPLE CARTRIDGES BY GC-NPD

#### Introduction

This method is suitable for up to 2 g charcoal cartridges. The charcoal is sonicated in extraction solvent and then filtered through a syringe filter for analysis by gas chromatography with nitrogen-phosphorus detection (NPD, also known as thermionic specific detector TSD).

The following extraction method has been previously validated for use in MITC air sampling studies. Refer to the following projects:

FEQL-NG-0605, MITC residential community air assessment; south Franklin County, WA;  
FEQL-1106 Optimizing fumigant efficacy while minimizing off-target volatile emissions;  
FEQL-1207 Near Field Emissions of MITC Following Shank Injection and Chemigation Metam Applications;  
FEQL-0708 Quantification of MITC in Activated Charcoal Air Cartridges from Two Chemigated Circles in Eastern Washington State.

#### Method

1. Remove a set of charcoal air samples from the -80°C freezer. Immediately after taking the samples from the freezer, remove at least one cap from the end of the sample cartridge to prevent pressure build-up in the cartridge. Place the sample cartridge in a labeled Corex<sup>®</sup> tube to contain any spills and allow samples to warm to room temperature.
2. For each analytical set, prepare at least one fortified recovery sample by adding a known amount of MITC solution (in methanol) to an appropriate size cartridge. Fortification levels will range from the methods limit of quantitation (LOQ, 0.25 µg MITC) to concentrations that exceed the highest residues encountered.
3. For each analytical set, include a control, blank cartridge of the appropriate size.
4. Carefully empty the contents of each cartridge (glass wool, plug, and charcoal) into labeled 25 mL screw-cap Corex<sup>®</sup> tubes.
5. Add 5 mL extraction solvent (80/20 mixture of ethyl acetate/carbon disulfide) to each tube by volumetric pipette or other accurate means, and then seal and place tube on ice (the solvent-charcoal interaction is exothermic). Prepare the extraction solvent in one liter batches by individually adding 800 mL of ethyl acetate to 200 mL carbon disulfide using graduated cylinders. Store the extraction solvent in a one-liter, screw-cap glass bottle in the dark when not in use to avoid decomposition of carbon disulfide.
6. Sonicate the samples for ca. two minute in a water-filled sonic bath (e.g. VWR AquaSonic<sup>®</sup>). After sonication, chill the samples in ice before filtering. Vortex samples.
7. Use a disposable glass Pasteur pipet to transfer an aliquot (~1-2 mL) to a plastic syringe

fitted with a 0.45 µm Teflon membrane filter (Whatman®). Collect filtered sample in an appropriately labeled autosampler vial for analysis by gas chromatography (GC).

8. The determination of MITC will be performed by gas chromatography with nitrogen-phosphorus thermionic detection (NPD). Conditions for determination are as follows:

Instrument: A Varian Star 3400CX gas chromatograph (or equivalent) with nitrogen phosphorus detection (NPD) and 8200CX Autosampler will be used for residue detection and quantification. Integration of chromatographic data will be performed using Varian Star Chromatography Workstation software.

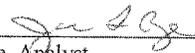
Column: EC-WAX, 15m x 0.53mm, 1.2 µm film thickness  
Carrier gas: Ultrapure helium, column flow rate 2-4 mL/min.  
Temperatures: Detector: 260°C  
Injector port: 55 to 225°C (rate: 250°C per min), hold for 5 min.  
Oven program  
Initial: 55°C, hold for 0.09min.  
Ramp 10°C/min to 90°C, hold for 5 min.

Injection volume: 2 µl  
Retention time: MITC retention time is based on the observed retention times of external calibration standards in each set and dependent upon instrument used.

Detector Gases: Typical NPD detector gas flows will be set at approximately 3-4 mL/min hydrogen, ca. 170 mL/min air, and 25-30 mL/min makeup gas. The NPD bead current will be adjusted as necessary from 3.0 to 3.6 A.

9. MITC residue concentrations will be calculated using external MITC linearity standards dissolved in the 80/20 ethyl acetate/carbon disulfide solvent mixture. A standard curve will be generated for each analytical set and all samples will be bracketed with MITC calibration standards.

Submitted by:

  
\_\_\_\_\_  
Jane LePage, Analyst

9-8-08  
Date

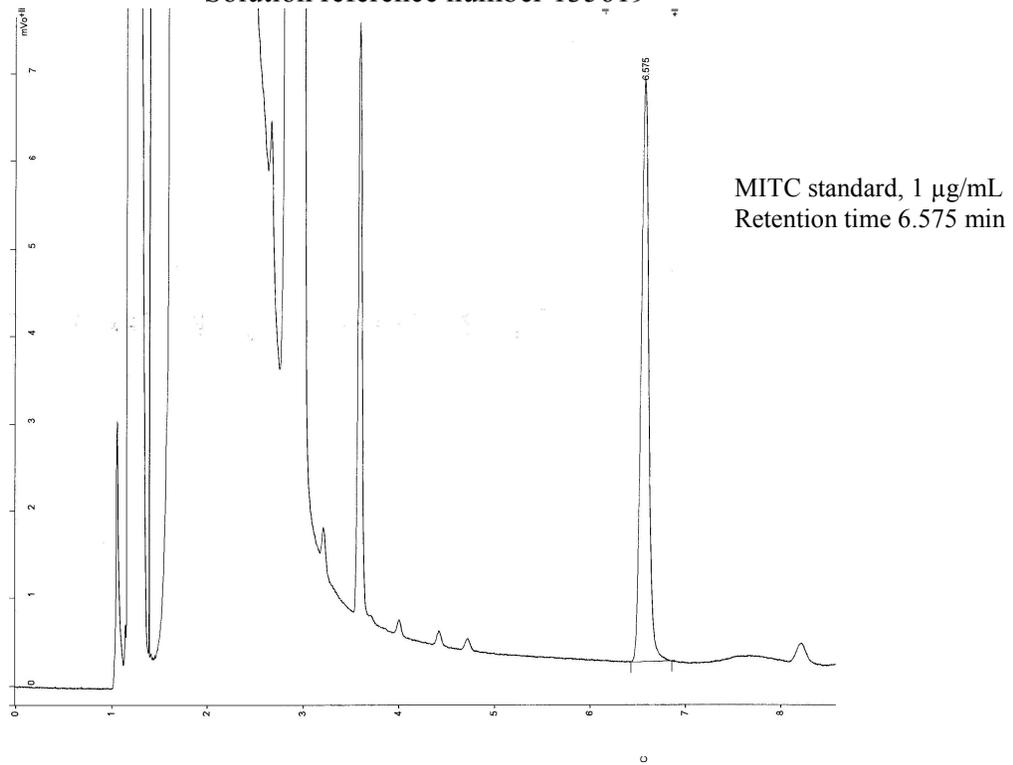
Approval:

  
\_\_\_\_\_  
Vincent R. Hebert  
Project Coordinator

9-8-08  
Date

**APPENDIX F: Representative Chromatograms**

**Figure 8**  
 MITC linearity standard, 1 µg/mL  
 Solution reference number 135619

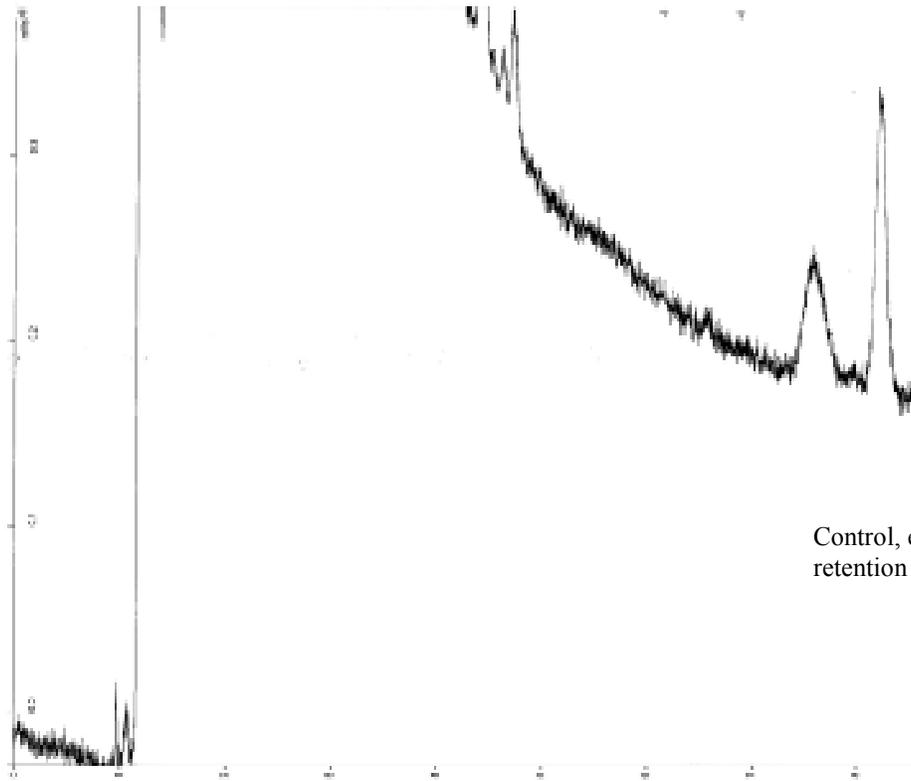


Peak No.	Peak Name	Result (ng)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	1/2 (sec)	Status Codes
1	MITC	100.0000	6.575	0.006	37035	BB	5.1	
Totals:		100.0000		0.006	37035			

Total Unidentified Counts : 0 counts

Detected Peaks: 1 Rejected Peaks: 0 Identified Peaks: 1

**Figure 9**  
 Control, 600 mg cartridge  
 Sample ID: 0808C31



Control, expected MITC  
 retention time 6.57 min

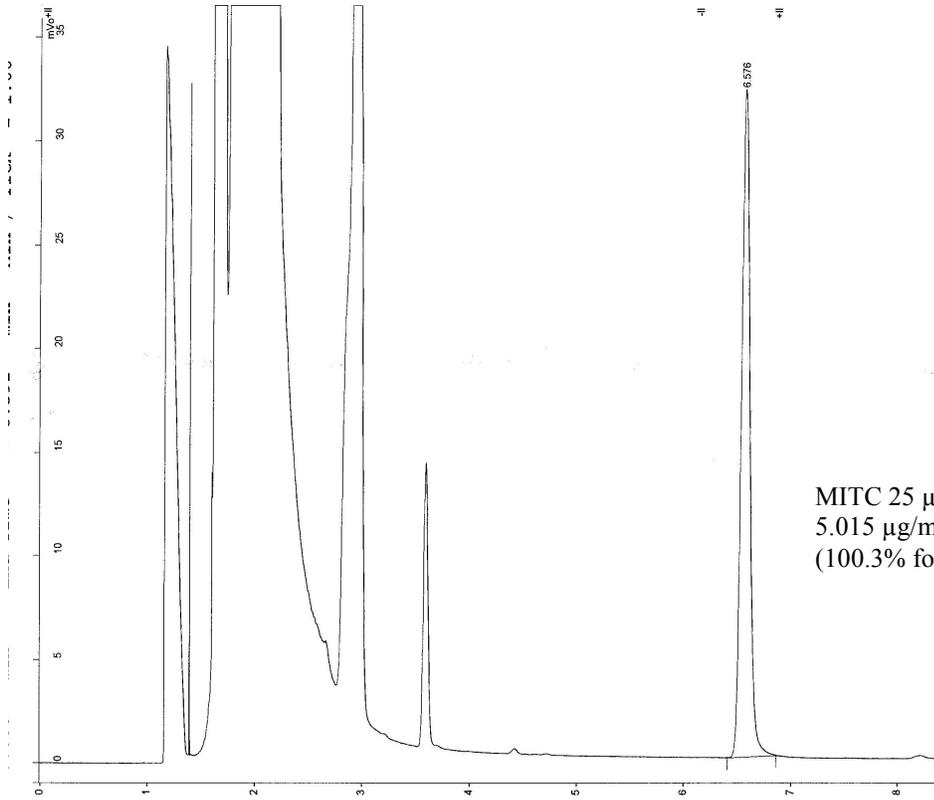
Peak No.	Peak Name	Result (ng)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
Totals:		0.0000		0.000	0			

Total Unidentified Counts : 0 counts

Detected Peaks: 0 Rejected Peaks: 0 Identified Peaks: 0

Multiplier: 1 Divisor: 1 Unidentified Peak Factor: 0

**Figure 10**  
 Fortified sample, 600 mg cartridge  
 Sample ID: 0808FS77



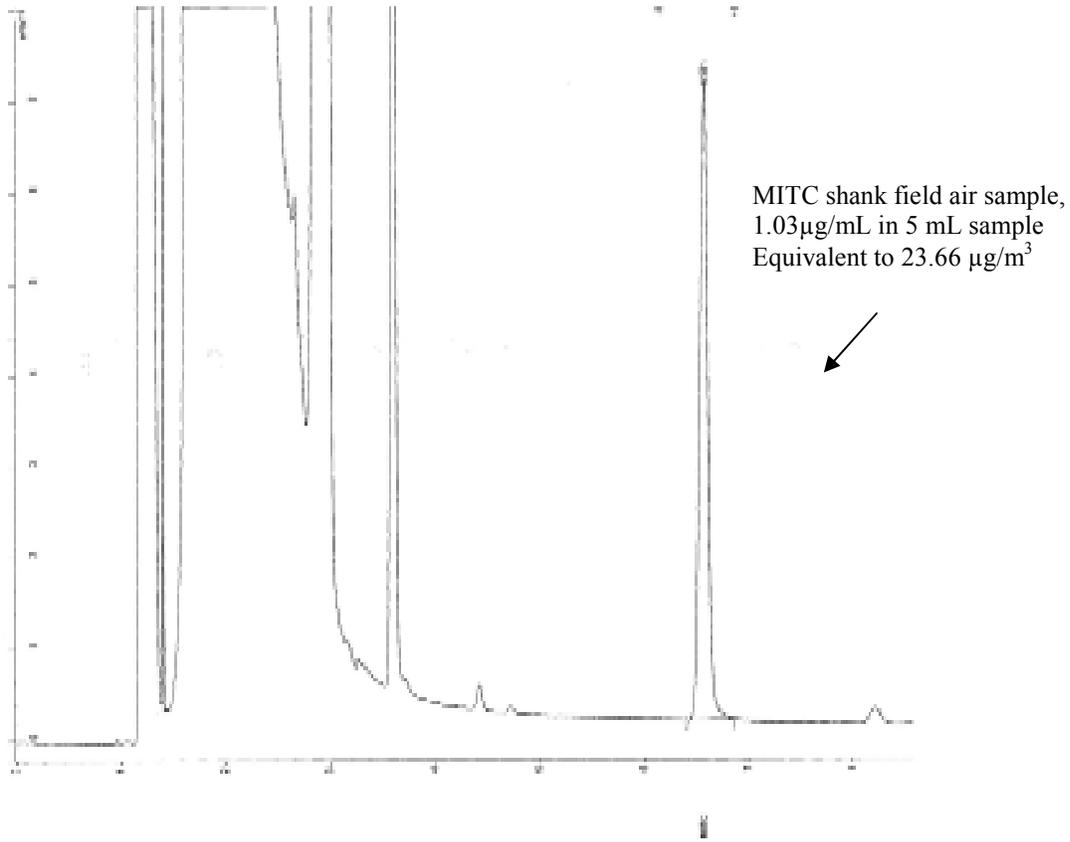
Peak No.	Peak Name	Result (ng)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1	MITC	100.0000	6.576	0.007	180764	BB	5.1	
Totals:		100.0000		0.007	180764			

Total Unidentified Counts : 0 counts

Detected Peaks: 1                      Rejected Peaks: 0                      Identified Peaks: 1

**Figure 11**

Shank Injection Sample, 1 g cartridge  
 Sample ID: SH6-D-101008



Peak No.	Peak Name	Result (ng)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1	MITC	100.0000	6.581	0.012	38540	BB	5.1	
Totals:		100.0000		0.012	38540			

Total Unidentified Counts : 0 counts

Detected Peaks: 1 Rejected Peaks: 0 Identified Peaks: 1

APPENDIX G: Estimated Field Emissions and Flux Assessment Methods

A. Estimated Field Emissions: Drizzle Boom

Period            CSAT3            Emissions Method Used            Loss Rates            Application Rate

Period	CSAT3	Emissions Method Used	Loss Rates	Application Rate
1	172.08	DPR Regression	6.56%	70.59 gal/acre
2	171.80	DPR Regression	3.27%	
3	67.00	DPR Regression	5.11%	
4	40.10	Mean Measured/Mean Modeled	3.06%	
5	35.32	Least Squares	2.69%	
6	32.20	DPR Regression	3.07%	
7	26.71	DPR Regression	2.04%	
8	57.15	DPR Regression	4.36%	
9	37.92	DPR Regression	2.17%	
10	26.83	DPR Regression	2.04%	
11	22.60	DPR Regression	1.72%	
12	15.29	DPR Regression	1.17%	
13	15.45	DPR Regression	0.88%	
14	31.90	DPR Regression	2.43%	
15	16.03	DPR Regression	2.44%	
16	9.73	Least Squares	1.67%	
17	4.40	Mean Measured/Mean Modeled	0.67%	
18	6.92	Mean Measured/Mean Modeled	0.92%	
19	3.14	Mean Measured/Mean Modeled	0.48%	
20	3.28	Adj. Least Squares	0.31%	

Total Loss Rate            47.05%

B. Estimated Field Emissions: Shank Injection

Period	CSAT3	Emissions Method Used	Loss Rates	Application Rate
1	6.56	Mean Measured/Mean Modeled	0.17%	51.67 gal/acre
2	12.48	Mean Measured/Mean Modeled	0.65%	
3	9.08	Mean Measured/Mean Modeled	0.95%	
4	12.21	Mean Measured/Mean Modeled	1.27%	
5	11.16	Mean Measured/Mean Modeled	1.16%	
6	16.22	Mean Measured/Mean Modeled	2.11%	
7	5.07	Least Squares	0.40%	
8	6.17	DPR Regression	0.64%	
9	5.43	DPR Regression	0.57%	
10	3.88	DPR Regression	0.40%	
11	3.42	DPR Regression	0.36%	
12	2.40	Least Squares	0.25%	
13	3.49	Least Squares	0.36%	
14	3.68	DPR Regression	0.38%	
15	5.84	Mean Measured/Mean Modeled	1.06%	
16	2.78	Mean Measured/Mean Modeled	0.65%	
17	0.91	Least Squares	0.17%	
18	2.14	Least Squares	0.45%	
19	1.39	Mean Measured/Mean Modeled	0.33%	
20	2.17	Mean Measured/Mean Modeled	0.23%	

Total Loss Rate      12.55%

## APPENDIX G (con't)

### C. Flux Assessment Methods

#### **DPR Emissions Assessment Methods**

**The associated spreadsheet, called “RESULT.XLS”, presents the actual estimated emission fluxes for each modeled period. The following discussion summarizes the technical steps involved with that emission estimation process.**

1. All measured and modeled data are used to calculate emission rates using linear regression.
2. If there are fewer than three pairs of measured and modeled values greater than 0.1 micrograms/cubic meter for both terms, there are not enough data pairs to estimate emission rates for the period. The emission rate for the period in question is defaulted by weighted interpolation or conservative diurnal matching. In addition, the standard error (used to compute distributions) is computed by multiplying the emission rate by a conservative default coefficient of variance of 0.3<sup>1</sup>
3. If there are at least three pairs of measured and modeled concentrations greater than 0.1 micrograms / cubic meter for both terms, linear regression (including both slope and intercept terms) is used to estimate emission rates by the best-fit line for the data. The slope of the linear regression line and the intercept term are checked for significance at the 95<sup>th</sup> percent confidence level.
  - 3a If the linear regression slope is significantly greater than zero at the 95<sup>th</sup> percent confidence level (range of emission rates in the 95<sup>th</sup> confidence interval does not include zero) and the intercept is not significantly different from zero at the 95<sup>th</sup> percent confidence level, the regression slope is used as the emission rate and the standard error of the slope is used as the standard error term for calculating the distribution of emission rates.
  - 3b If the linear regression slope is significant, but the intercept is significantly different from zero at the 95<sup>th</sup> percent confidence level, then linear regression without an intercept term (least squares) is used and the slope computed on that basis is checked for significance.

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<sup>1</sup> A coefficient of variance of 0.3 is used as a conservative default consistent with Cullen & Frey, Probabilistic Techniques in Exposure Assessment, Plenum Press, New York, 1999, pp. 66-67.

- If the least squares slope without an intercept is not significant at the 95<sup>th</sup> percent confidence level, then the mean measured divided by the mean modeled method is used to calculate the emission rate for this period. The standard error is set to the emission rate multiplied by the default coefficient of variance (0.3).
  - If the least squares slope without an intercept is significant, then the least squares slope without an intercept is used as the emission rate for this period and the standard error of the slope is used as the standard error term for calculating the distribution of emission rates.
- 3c If the linear regression slope is not significant, the slope term cannot be used. The least squares regression method (linear regression without an intercept term) is used and the slope checked for significance.
- If the least squares slope without an intercept is not significant at the 95<sup>th</sup> percent confidence level, then the mean measured divided by the mean modeled method is used to calculate the emission rate for this period. The standard error is set to the emission rate multiplied by the default coefficient of variance (0.3).
  - If the least squares slope without an intercept is significant, then the least squares slope is used as the emission rate for this period and the standard error of the slope is used as the standard error term for calculating the distribution of emission rates.

A flow chart describes the above process concisely as shown below.

