# ESTIMATION OF EXPOSURE OF PERSONS IN CALIFORNIA TO METHYL ISOTHIOCYANATE

by

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HS-1806

September 30, 2003

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## EXECUTIVE SUMMARY

Methyl isothiocyanate (MITC) has been used extensively in California to control weeds, soil-borne diseases, and nematodes in soil. Most MITC used in pest control is generated from the use of metam-sodium. As of September 2003, there were two active registrations of MITC products in California. Total reported use of MITC products in 2001 was 2,871 pounds. MITC is also the major degradate of metam-sodium after soil application. As of September 2003, there were 23 metam-sodium products registered in California. The estimated annual average MITC produced from the use of metam-sodium products (1997-2001) was approximately 8.5 million pounds. Dazomet and potassium N-methyldithiocarbamate (metam-potassium) can also generate MITC. In 2001, total reported use of dazomet was 44,299 pounds of active ingredient. The total amount of MITC generated from dazomet was about 0.29% of the total MITC produced from the use of metam-sodium. In 2001, use of potassium N-methyldithiocarbamate was 96,753 lbs.

From 1990 through 2001, the annual average illness/injury cases classified as definitely, probably, and possibly attributed to exposure to metam-sodium/MITC were 5.9, 21.9, and 6.1, respectively. The overall annual average illnesses/injuries for the same period was 33.9 cases. These cases excluded illnesses/injuries as a result of the Cantara spill in 1991 where a train tanker spilled metam-sodium into the Sacramento River. In 1993, there were two illnesses/injuries attributed to exposure to metam-sodium/MITC in combination with other pesticides.

Handlers, including loaders, applicators, or loaders/applicators, of metam-sodium can be exposed to airborne MITC during soil fumigation. Two studies conducted or sponsored by the Metam Sodium Task Force (MSTF) were used to determine exposure levels of handlers to MITC during soil fumigation of metam-sodium. The short-term exposure of adult male handlers to MITC ranged from 64 to 818 parts per billion (ppb) for 1-hour MITC concentrations and those for 8-hour MITC ranged from 41 to 515 ppb. In addition, absorbed daily dosage (ADD), seasonal

average daily dosage (SADD), and annual average daily dosage (AADD) were also determined for adult handlers.

Residents can also be exposed to ambient MITC in residential areas from off-site (application site) movement of MITC from nearby fumigated fields. Six studies were conducted or sponsored by California Air Resources Board (CARB), University of Nevada, University of California, MSTF, and the Department of Pesticide Regulation (DPR) to determine potential exposure levels of residents to MITC in air. The exposures derived from the off-site MITC monitoring study sponsored by the MSTF (MSTF, 1999b) are essentially underestimated because not all sampling stations were located in the downwind direction. The overall short-term (24- or closest to 24-hour) off-site MITC concentrations for various distances from the treated fields, ranged from 5.5 to 1,102 ppb. Absorbed dosages were also estimated for adult males and females, and children as ADD, SADD, and AADD. One- and 8-hour off-site MITC concentrations were also determined. Depending on the distance from the treated fields and the applications methods, the overall 1-hour MITC concentrations from the studies (excluding the study using drip irrigation) ranged from 15 to 2,853 ppb, and those for 8-hour MTIC ranged from 8.3 to 2,348 ppb. Essentially, MITC concentrations obtained from the off-site air monitoring study following the application of metam-sodium by drip irrigation (Krieger *et al*., 1998) are lower than those obtained from studies using other application methods. However, direct comparisons of data could not be made because samples were collected from different distances of treated fields.

Three studies (CARB, 1994a; Seiber *et al*., 1999; DPR, 2003b) were conducted to determine ambient MITC concentrations. The overall mean for short-term (24- or closest to 24-hour) ambient MITC concentrations ranged from 0.25 to 8.76 ppb. One-hour ambient MITC concentrations ranged from 0.3 to 14.6 ppb. The same range of MITC concentrations was also observed for 8-hour MITC. Absorbed dosages were also estimated for adult males and females, and children as ADD, SADD, and AADD.

MITC is in risk assessment because it has been shown to cause eye irritation for acute toxic effects in human subjects and pulmonary irritation for subchronic and chronic toxic effects in rats. This report was prepared as part of the Department's risk assessment process for MITC.

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## INTRODUCTION

This human exposure assessment document provides essential information for the risk assessment of methyl isothiocyanate (MITC). This document was prepared as part of the Department's risk assessment process. It will also be used as a basis for mitigation proposals if exposures to MITC are found to cause excessive risks.

The exposure estimates for handlers (loaders, applicators) and residents (and bystanders) were obtained from monitoring air in the worker's breathing zone, off-site air concentrations during and after soil applications of metam-sodium, and ambient air. In addition to exposure estimates, presentation of other properties of MITC is necessary for a better understanding of its nature, usage, and effects. These additional categories are: physical and chemical properties, DPR and U.S. EPA regulatory history, formulations/label precautions, usage, illnesses/injuries, dermal toxicity and eye irritation, dermal/inhalation absorption, and animal metabolism.

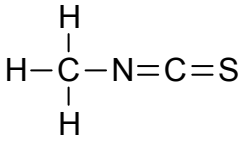
A major portion of this exposure document was adopted from the report HS-1704 (Thongsinthusak, 2001), which was prepared under the requirements of the Toxic Air Contaminant Act. HS-1704 was previously reviewed by the Worker Health and Safety Branch (WH&S), the Scientific Review Panel, and the public. Data or information added to this document (HS-1806) as compared to HS-1704 are three handler exposure studies, one off-site air monitoring study from drip irrigation of metam-sodium in untarped and partially tarped fields, exposure estimates determined for annual average daily dosages. Also, sections on Executive Summary, Usage, and Illness/Injury Data are updated.

## PHYSICAL AND CHEMICAL PROPERTIES

(Degussa Corporation, 1988a)

| | | |
|---|---|---|
| 1. | Chemical name: | Methyl isothiocyanate |
| 2. | Common names: | MITC, Methyl Mustard Oil |
| 3. | Trade names: | Degussa Methylisothiocyanate, Vorlex®, Trapex® |
| 4. | CAS registry number: | 556-61-6 |

5. Structural formula:



| | | |
|---|---|---|
| 6. | Empirical formula: | $C_2H_3NS$ |
| 7. | Molecular weight (MW): | 73.1 |
| 8. | Physical state: | Solidified melt |
| 9. | Density: | 1.07 g $cm^{-3}$ at 37 $^oC$ |
| 10. | Odor: | Pungent, similar to horseradish |
| 11. | Color: | Yellowish |
| 12. | Boiling point: | 119 $^oC$ |
| 13. | Melting point: | 34 $^oC$ |
| 14. | pH: | 6 (at a concentration of 5 g/L water) |
| 15. | Flash point: | The "flash point" of the solidified melt is about 23-30 $^oC$. |
| 16. | Solubility: | Poorly soluble in water, it is readily soluble in all common organic solvents like acetone, ethanol, benzene, cyclohexanone, dichloromethane, light petroleum, etc. |
| 17. | Vapor pressure: | 2.13 kPa (16.0 torr or 16 mmHg) at 25 $^oC$ (Tomlin, 1997) |
| 18. | Octanol/Water partition coefficient: | 19 |
| 19. | Corrosion characteristics: | Corrosive to iron, zinc, polyvinyl chloride, and rubber. |

## DPR AND U.S. EPA REGULATORY HISTORY

The United States Environmental Protection Agency (U.S. EPA) listed outstanding data requirements for reregistration of MITC (U.S. EPA, 1991). Additional studies required included: physical and chemical properties; acute and long-term toxicity; residues in plants, soil, food and feed; residue dissipation; and human exposures. Subsequent to the 1991 listing of the extensive reregistration requirements, MITC was declared by the U.S. EPA to be a "non-food" use pesticide, so the longer-term animal study requirements were dropped.

The U.S. EPA has initiated the risk assessment of MITC. It is anticipated that their draft document will be ready for public comment by March 2004. DPR is developing a mitigation proposal for acute off-site MITC exposures to residents and by standers, in accordance with a risk management directive (Gosselin, 2002).

## FORMULATIONS/LABEL PRECAUTIONS

Formulations

In California, there are two registered MITC products for wood preservative use: MLPC Methylisothiocyanate and Osmose MITC-Fume™ Fungicide for Wood (DPR, 2003a). Metam-

sodium, which can generate MITC, is registered mainly as a soil fumigant. As of September 2003, there were 23 metam-sodium products registered in California (DPR, 2003a).

Label Precautions

The two MITC products are Toxicity Category I pesticides that have a signal word "POISON/DANGER." The products are restricted use pesticides due to high acute toxicity. Special precautionary statements include: fatal if inhaled or absorbed through skin; may be fatal if swallowed; corrosive; causes irreversible eye damage and skin burns; when applied in enclosed areas, wear a mask or pesticide respirator jointly approved by the Mining Enforcement and Safety Administration and National Institute for Occupational Safety and Health; wear goggles, safety glasses or face shield, protective clothing, and rubber gloves. Wash thoroughly after handling, before eating or smoking. Remove contaminated clothing and wash before reuse.

## USAGE

MITC is a general biocide used to control weeds, soil-borne diseases, nematodes in soil, and wood fungi. Currently in California, MLPC Methylisothiocyanate and Osmose MITC-Fume™ Fungicide for Wood are the only two commercial products that contain MITC as an active ingredient (AI) (DPR, 2003a). MITC can be generated from other pesticides, such as metam-sodium, dazomet, and potassium N-methyldithiocarbamate (metam-potassium). Most MITC used in pest control for agricultural production is generated from metam-sodium applied to soil by various methods.

As a wood preservative pesticide, commercial MITC products are intended for use as a remedial treatment in large structural timbers such as utility poles, piling, bridge timbers, and laminated wood products. For the application, a tube containing MITC is opened and inserted into pre-drilled holes in the pole, setting the opening side of the tube downwards. Then, the hole is plugged with a tight fitting treated wooden dowel.

Conversion of metam-sodium to MITC

Leistra and Crum (1990) conducted a study to determine an emission rate of MITC into the air after application of metam-sodium in greenhouse soil. Metam-sodium was applied with a small self-propelled shank injector (hand-operated). The treated area was covered with low density polyethylene film (30 μm) for seven days. MITC in the air was sampled for a period of 14 days. The total emission of MITC measured in mass unit after 14 days was determined to be 60% of the dosage of metam-sodium. This emission rate is similar to the transformation rate of metam-sodium to MITC based on mole per mole conversion, which is about 57% by weight (73.1, MW of MITC x 100/129.2, MW of metam-sodium).

The estimated quantities of MITC from MITC products and MITC generated from metam-sodium products from 1997 to 2001 in California are shown in Table 1.

Table 1. Use and estimated total production of MITC in California between 1997-2001.

| | | Amount of MITC (million pounds, lbs) | | |
|---|---|---|---|---|
| Year | Use of metam-sodium[a] | MITC generated from metam-sodium[b] | MITC products | Total MITC |
| 1997 (DPR, 1999b) | 15.0 | 9.0 | $0.40 \times 10^{-3}$ | 9.0 |
| 1998 (DPR, 2000a) | 14.0 | 8.4 | $0.22 \times 10^{-3}$ | 8.4 |
| 1999 (DPR, 2000b) | 17.3 | 10.4 | $0.62 \times 10^{-3}$ | 10.4 |
| 2000 (DPR, 2001) | 12.8 | 7.7 | $3.3 \times 10^{-3}$ | 7.7 |
| 2001 (DPR, 2002) | 11.3 | 6.8 | $2.9 \times 10^{-3}$ | 6.8 |
| Average (1997-2001) | 14.1 | 8.5 | $1.36 \times 10^{-3}$ | 8.5 |

[a] Metam-sodium (million pounds) from the annual use reports of DPR.

[b] Pounds of MITC generated from metam-sodium = 60% x ([a]) (Leistra and Crum, 1990).

In 2001, total reported use of dazomet was 44,299 lbs AI (DPR, 2002). In the presence of moisture in soil, dazomet undergoes degradation to methyl(methylaminomethyl)-dithiocarbamic acid, which then undergoes further degradation to MITC, formaldehyde, hydrogen sulfide, and methylamine (Tomlin, 1997). The total amount of MITC generated from the use of dazomet in 2001 is estimated so that it can be compared with the total amount of MITC generated from metam-sodium and potassium N-methyldithiocarbamate in the same year. To illustrate the total production of MITC from dazomet in 2001, it is assumed that the conversion from dazomet to MITC is based on mole per mole basis similar to the conversion of metam-sodium to MITC. In 2001, the total amount of MITC generated from dazomet was estimated to be 19,952 lbs [(73.1 (MITC MW) x 44,299 lbs dazomet (use in 2001)) ÷ 162.3 (dazomet MW) = 19,952 lbs MITC]. The total amount of MITC produced from dazomet was about 0.29% of the total MITC produced from metam-sodium. Therefore, exposure of workers and residents to MITC generated from dazomet is insignificant compared to MITC generated from metam-sodium. In 2001, use of potassium N-methyldithiocarbamate was 96,753 lbs (DPR, 2002).

## ILLNESS/INJURY DATA

In California, there was no separate classification of illnesses/injuries resulting from exposure to MITC alone. It was assumed that the majority of illnesses/injuries associated with metam-sodium exposure were caused by exposure to MITC because it is the major degradate of metam-sodium after application to soil and it is volatile in the environment. From 1990 to 2001, there were 407 illnesses/injuries (annual average 33.9 cases) attributed to exposure to metam-sodium/MITC as reported by physicians in California (Mehler, 2003) (Table 2). These illnesses/injuries were classified according to relationship to exposure. The majority of illness/injury cases from 1990 to 2001 occurred to workers during field fumigation and to residents following off-site movement of MITC (classified as non-occupational exposure) (Table 3). These illness/injury cases were also grouped according to symptoms experienced by affected persons (Table 4). These cases excluded illnesses/injuries as a result of the Cantara spill in 1991 where a train tanker spilled metam-sodium into the Sacramento River.

Table 2. Case reports received by the California Pesticide Illness Surveillance Program in which health effects were attributed to exposure to metam-sodium/MITC (1990-2001): Classified according to relationship to exposure.[a]

| | Illness/injury relationship | | | |
|---|---|---|---|---|
| Year | Definite[b] | Probable[c] | Possible[d] | Total |
| 1990 | 6 | 6 | 8 | 20 |
| 1991 | 2 | 2 | 9 | 13 |
| 1992 | 1 | 9 | 8 | 18 |
| 1993 | 14 | 4 | 0 | 18 |
| 1994 | 4 | 5 | 1 | 10 |
| 1995 | 27 | 20 | 1 | 48 |
| 1996 | 9 | 43 | 4 | 56 |
| 1997 | 5 | 12 | 3 | 20 |
| 1998 | 0 | 2 | 2 | 4 |
| 1999 | 1 | 149 | 33 | 183 |
| 2000 | 2 | 6 | 2 | 10 |
| 2001 | 0 | 5 | 2 | 7 |
| Total | 71 | 263 | 73 | 407 |
| Average | 5.9 | 21.9 | 6.1 | 33.9 |

[a] In 1993, there were two illnesses/injuries attributed to exposure to metam-sodium/MITC in combination with other pesticides. Thus, there were altogether 409 illness/injury cases from 1990 to 2001. These cases excluded illnesses/injuries as a result of the Cantara spill in 1991 where a train tanker spilled metam-sodium into the Sacramento River.

[b] The "definite" classification indicates the signs and symptoms exhibited by the affected person are such that would be expected to result from the exposure described.

[c] The "probable" classification indicates that there is close correspondence between the exposure and the illness experienced.

[d] The "possible" classification indicates some correspondence between the exposure described and the illness/injury experienced.

Table 3. Case reports received by the California Pesticide Illness Surveillance Program in which health effects were attributed to exposure to metam-sodium/MITC (1990-2001): Classified according to activities.[a]

| Activity | 1990 | 1991 | 1992 | 1993 | 1994 | 1995 | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Loader | 0 | 1 | 1 | 3 | 3 | 3 | 3 | 5 | 0 | 0 | 1 | 0 | 20 |
| Applicator | 1 | 0 | 0 | 2 | 0 | 1 | 3 | 2 | 2 | 0 | 3 | 5 | 19 |
| Fumigation, field | 14 | 7 | 1 | 1 | 3 | 0 | 0 | 5 | 1 | 2 | 0 | 0 | 34 |
| Drift: Occupational | 2 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 8 | 0 | 0 | 12 |
| Non-occup. | 0 | 0 | 11 | 11 | 0 | 40 | 48 | 0 | 1 | 167 | 6 | 0 | 284 |
| All others | 3 | 5 | 5 | 1 | 4 | 4 | 0 | 8 | 0 | 6 | 0 | 2 | 38 |
| Total | 20 | 13 | 18 | 18 | 10 | 48 | 56 | 20 | 4 | 183 | 10 | 7 | 407 |

[a] In 1993, there were two illnesses/injuries attributed to exposure to metam-sodium/MITC in combination with other pesticides. Thus, there were altogether 409 illness/injury cases from 1990 to 2001. These cases excluded illnesses/injuries as a result of the Cantara spill in 1991 where a train tanker spilled metam-sodium into the Sacramento River.

Table 4. Case reports received by the California Pesticide Illness Surveillance Program in which health effects were attributed to exposure to metam-sodium/MITC (1990-2001): Classified according to symptoms.[a, b]

| Year | Systemic | Skin | Eye & Eye/skin | Respiratory & Respiratory/eye | Total |
|---|---|---|---|---|---|
| 1990 | 8 | 11 | 1 | 0 | 20 |
| 1991 | 4 | 6 | 1 | 2 | 13 |
| 1992 | 8 | 4 | 5 | 1 | 18 |
| 1993 | 10 | 6 | 2 | 0 | 18 |
| 1994 | 3 | 6 | 1 | 0 | 10 |
| 1995 | 40 | 2 | 6 | 0 | 48 |
| 1996 | 22 | 6 | 28 | 0 | 56 |
| 1997 | 10 | 9 | 1 | 0 | 20 |
| 1998 | 2 | 1 | 1 | 0 | 4 |
| 1999 | 161 | 18 | 4 | 0 | 183 |
| 2000 | 7 | 1 | 2 | 0 | 10 |
| 2001 | 4 | 3 | 0 | 0 | 7 |
| Total | 279 | 73 | 52 | 3 | 407 |
| Average | 23.3 | 6.1 | 4.3 | 0.3 | 33.9 |

[a] In 1993, there were two illnesses/injuries attributed to exposure to metam-sodium/MITC in combination with other pesticides. Thus, there were altogether 409 illness/injury cases from 1990 to 2001. These cases excluded illnesses/injuries as a result of the Cantara spill in 1991 where a train tanker spilled metam-sodium into the Sacramento River.

[b] Examples of reported symptoms were: eye - watery, burning, itchy, blurred vision; skin - rash, burns, redness, swelling; systemic - nausea, chest pain, scratchy throat, diarrhea, weakness, dizziness, headache, malaise, salivation, vomiting; respiratory - cough, shortness of breath.

## DERMAL TOXICITY/EYE IRRITATION

Dermal/eye irritation

A dermal irritation study was conducted in one male and two female New Zealand white rabbits using technical MITC (97% AI). Each animal was exposed to 0.5 mL technical MITC (heated to 40 $^{o}$C to liquefy). All animals died about one hour after the exposure. Skin showed severe erythema and slight edema at one hour post dosing (Degussa Corporation, 1988b).

A primary eye irritation study was conducted in one male and two female New Zealand white rabbits using technical MITC (97% AI). Each animal was exposed to 0.1 mL technical MITC (heated to 40 $^{o}$C to liquefy). The results showed that MITC caused a primary eye irritation in rabbits under conditions specified in this study (Degussa Corporation, 1988c). Symptoms included corneal opacity, redness, chemosis and ocular lesion. MITC is also corrosive to eyes of rabbits. Because of the severity of the symptoms, the test was terminated after an observation period of 72 hours.

Irritant effects of MITC on rabbit eye mucosa were reported (Nor-Am Agricultural Products, 1983). A single instillation of 100 mg of test compound into the lower lid of the rabbits' eyes produced severe inflammation including corneal opacity, iritis, and conjunctival swelling.

Acute human health effects

In a study designed to determine the human no-effect level for MITC-induced eye irritation, volunteers were exposed to MITC vapors for up to eight hours (Russell and Rush, 1996; DPR, 1996b). The vapor was directed only to the subjects' eye-area through the use of specially designed goggles. The no-effect air concentration levels ranged from 3.3 ppm after a 1-minute exposure to 0.22 ppm for exposure between 1 and 2 hours.

Dermal sensitization

Young adult male, Hartley strain guinea pigs were induced with non-irritating doses of metam-sodium (1% Vapam® technical in deionized water, ICI Americas Inc., 1988). The induction period was 6 hours for each application. There were a total of ten applications, which were applied on alternate days. The animals were challenged on days 35, 42, and 49 with non-irritating doses of MITC (0.1% in acetone). The results from the study showed that MITC at a non-irritating dose had the potential to produce dermal sensitization reactions under the experimental conditions specified in the study.

## DERMAL/INHALATION ABSORPTION

A dermal absorption study of MITC is not available. It is assumed that the dermal dose of MITC vapor is negligible. Exposure of workers and residents to MITC vapor are estimated by monitoring ambient air concentrations. Monitoring of dermal exposure to MITC is extremely difficult, if not impossible.

There is no inhalation uptake/absorption study of MITC available. The absorbed dose of MITC is estimated from the default inhalation uptake/absorption. Because MITC has low molecular weight, moderate water solubility and high chemical reactivity, the absorption will be closer to 100% than the default 50% (Thongsinthusak *et al.*, 1993). The default inhalation uptake/absorption of MITC is assumed to be 100%.

## ANIMAL METABOLISM

Rats – Oral

A single-dose metabolism study in rats was available for review. In the environment, and after oral administration to animals, the major metam-sodium degradate is MITC. For this reason, a study of both metam-sodium and MITC was undertaken.

The metabolism study compared the absorption, tissue distribution, and excretion of metam-sodium and MITC (Hawkins *et al*., 1987). Rats were given radiolabeled metam-sodium (>99% pure) at 10 or 100 mg/kg, or MITC at 4.4 or 33 mg/kg by gastric gavage. Feces and urine samples were collected at 24-hour intervals up to 7 days. Expired air was collected at 24-hour intervals up to 3 days, passing through a series of 3 traps containing 2-ethoxyethanol (to trap MITC), 20% aqueous sodium hydroxide to trap carbon dioxide ($CO_2$), and Viles' reagent (to trap carbonyl sulphide (COS) and carbon disulfide ($CS_2$). Following doses of MITC, the radioactivity was principally eliminated in urine and in expired air (as carbon dioxide), and the proportions excreted by those routes were independent of dose. In contrast, following doses of metam-sodium, there was a greater excretion of radioactivity as carbon disulfide, and possibly carbonyl sulphide, and a lesser excretion in the urine. Moreover, excretion was dose dependent with metam-sodium, and at 100 mg/kg a significant proportion of an unidentified volatile metabolite was eliminated in exhaled air. This metabolite was retained in a trap designed to collect MITC, although MITC was not recovered in a similar trap following direct MITC administration to rats (Wagner, 1989). Excretions (% of dose) are listed in Table 5. Proposed degradation/metabolic pathways for metam-sodium and MITC are shown in Figure 1 (adopted from Rose, 1989).

Table 5. Excretion and retention of radioactivity (% of dose) following metam-sodium or MITC oral gavage to rats (n = 5 per dose).

| | Dose | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Metam-sodium[a] | | | | MITC[a] | | | |
| | 10 mg/kg | | 100 mg/kg | | 4.4 mg/kg | | 33 mg/kg | |
| | M | F | M | F | M | F | M | F |
| Tissues | 2.01 | 1.75 | 1.17 | 1.32 | 2.20 | 1.86 | 1.71 | 2.29 |
| Urine (0-168 hrs) | 52.02 | 58.09 | 37.34 | 42.42 | 84.43 | 86.36 | 87.09 | 85.57 |
| Cage washings | 0.10 | 0.05 | 0.06 | 0.04 | 0.15 | 0.07 | 0.18 | 0.15 |
| Feces (0-168 hrs) | 4.48 | 2.88 | 1.87 | 1.57 | 2.74 | 1.45 | 1.93 | 1.83 |
| Expired air (MITC trap) (0-72 hrs) | 0.45 | 1.26 | 24.53 | 24.04 | 0.95 | 1.51 | 0.72 | 1.67 |
| Expired air ($CO_2$) (0-72 hrs)[b] | 19.56 | 18.13 | 7.20 | 5.53 | 16.08 | 14.88 | 7.32 | 7.23 |
| Expired air (COS & $CS_2$) (0-72 hrs)[c] | 18.35 | 13.80 | 21.34 | 17.63 | 0.05 | 0.04 | 0.43 | 0.48 |
| Total recovery | 96.96 | 95.95 | 93.50 | 92.55 | 106.59 | 106.14 | 99.37 | 99.22 |

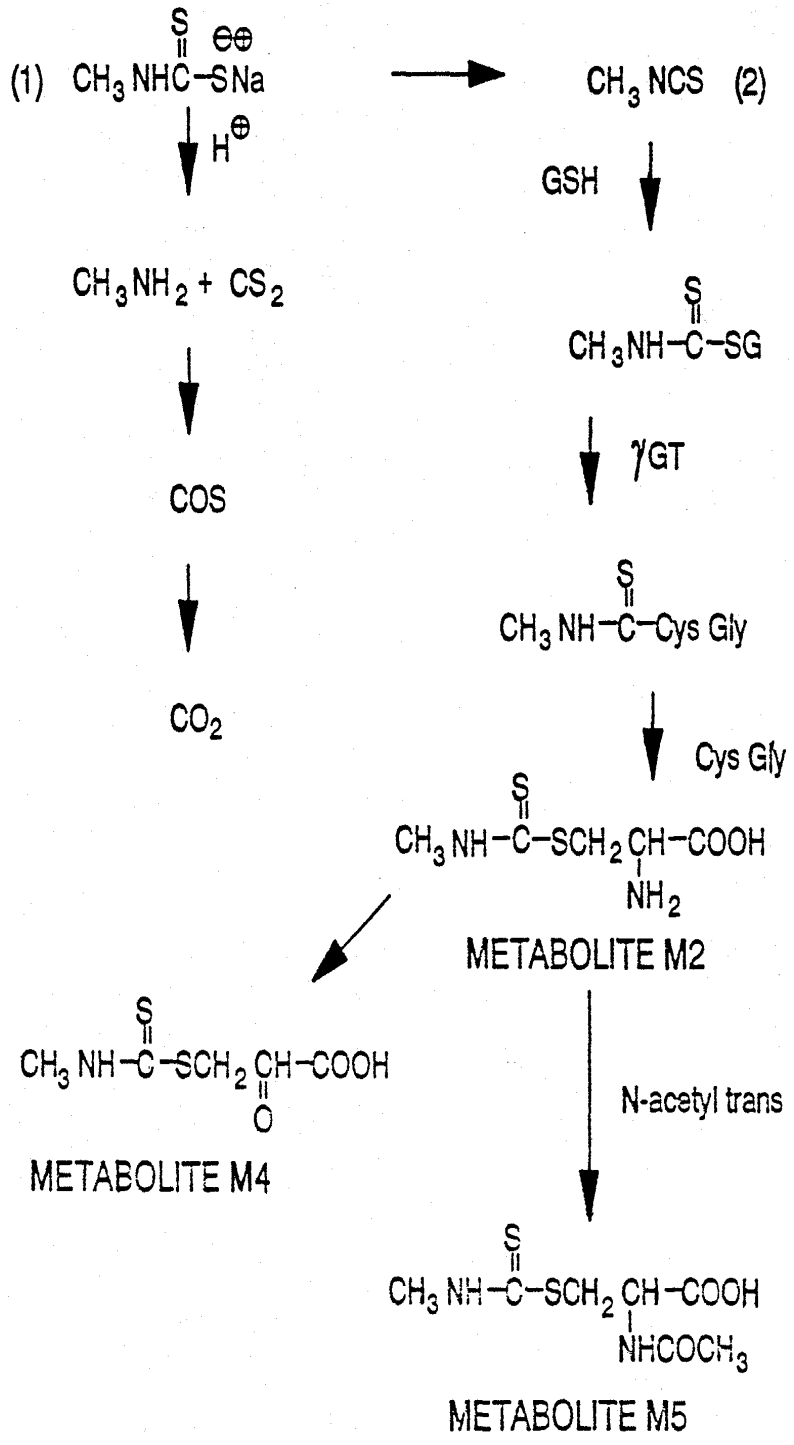
[a] Results in % of dose.
[b] $CO_2$ is carbon dioxide
[c] COS is carbonyl sulphide; $CS_2$ is carbon disulfide

Tissue content was highest in the thyroid on a μg/g basis at 168 hours. Kidneys and livers were among the sites with the highest retention of radioactivity, and along with the thyroid were thought to be the tissues responsible for metabolism and excretion. The investigators concluded

that the absorption was similar at both doses of metam-sodium, but with a somewhat different pattern of disposition. Rates of elimination of radioactivity in urine revealed that following MITC administration, radioactivity was principally detected during 0-8 h after dosing, whereas following metam-sodium administration it was eliminated at a slightly slower rate, in approximately equal amounts during 0-8 and 8-24 hrs. The difference in excretion rate was mirrored by a slower initial rate of elimination of radioactivity from the plasma of metam-sodium dosed animals. The same urinary metabolites were identified for both compounds although there were some differences in the relative proportions. Neither parent compound was present in the urine. A single major metabolite (M5) represented 16-25% of the dose for metam-sodium and 56-66% of the dose for MITC. There was only one other metabolite (M4) formed in appreciable amounts from both compounds, and represented 5-10% of the dose. There was no evidence for the presence of glucuronide or sulfate conjugates. The major metabolite (M5) was identified as N-acetyl-S-(N-methylthiocarbamoyl)-L-cysteine. The other metabolite (M4) was shown to correspond chromatographically to the cysteine conjugate. This study (Hawkins *et al*., 1987) was not acceptable to DPR due to variances from FIFRA guidelines such as lack of multiple dosing and analysis, stability, etc. of the dosing solutions.

It was suggested that the metam-sodium underwent acid hydrolysis in the stomach to form MITC and $CS_2$, but that a portion of the metam-sodium may have been absorbed intact. That would explain the slower excretion and the dose-dependent excretion compared with MITC (Wagner, 1989).

Figure 1. Proposed degradation/metabolic pathways for metam-sodium (1) and MITC (2).




Abbreviations: GSH is Glutathione S-transferase; γGT is γ-Glutamyltranspeptidase; N-acetyl trans is N-acetyltransferase; Cys Gly is Cysteinylglycinase.

## EXPOSURE ASSESSMENT

There are two different groups of exposure estimates for MITC: first, the exposure estimates for loaders and applicators (handlers or pest control operators); second, the exposure estimates for residents who live, work, or travel to places near treated fields. Data for the first exposure group were obtained from two studies conducted in Kern County (A.3; MSTF, 1999a and A.4; MSTF, 2001). These studies were conducted to measure airborne MITC during loading and application of metam-sodium. Participants of these studies observed the application procedures in the 1999 Technical Information Bulletin (TIB), *Guidelines for All Application Methods for Metam-Sodium in California*. (These guidelines were developed to minimize off-site movement of odors when applying metam-sodium and are required procedures in California.) Two other studies are presented in this document for historical perspective, only. These studies were conducted in Arizona (A.1; ICI America Inc., 1992) and Washington (A.2; Zeneca Inc., 1993a). While exposure values and margins of exposure were calculated, neither of these studies followed the current TIB guidelines. These studies represent extreme case exposure scenarios and may not be representative of appropriate application methods.

Data for the second exposure group were obtained from six studies. These studies were conducted by the California Air Resources Board (CARB) (B.2 (ambient); CARB, 1994a), the Department of Pesticide Regulation (DPR) (B.4 (off-site); Wofford *et al*., 1994 and B.8 (ambient); DPR, 2003b), the University of Nevada (B.7 (ambient); Seiber *et al.*, 1999), MSTF (B.9 (off-site); MSTF, 1999b), and the University of California, Riverside in cooperation with the University of Nevada (B.10 (off-site); Krieger *et al.*, 1998). These off-site MITC studies followed the requirement of the TIB, specifically the soil was "sealed" immediately following application to minimize off-site movement of odors. Four other studies are presented in this document for historical purposes, only. These studies were conducted by CARB (B.1 (off-site); CARB, 1993, B.3 (off-site); CARB, 1994b, Zeneca Inc. (B.5 (off-site); Zeneca, 1993b), and B.6 (off-site); CARB, 1997). While exposure values and margins of exposure were calculated, none of these studies followed the current TIB guidelines where the soil in these studies was not "sealed" following application, as is currently required. These studies represent extreme case exposure scenarios and may not be representative of appropriate application methods.

Scientists at DPR believe that the study (B.4) conducted by Wofford et al. (1994) followed practices that would be representative of practices described in the current TIB. The application occurred in the evening, and at a distance greater than one-half mile from an occupied structure. The soil type was Cerini loam. The current TIB specifies that one-quarter inch of water must be applied immediately following application to loamy soils. According to the study, watering-in occurred for 1.5 hours immediately following the application. The water delivery rate during the watering-in period was not reported; however, the delivery rate during application was reported as 5,680 liters/minute. Based on the reasonable assumption that the water delivery rate during the watering-in period was the same as the delivery rate during the application, more than one-quarter inch of water was applied during the watering-in period. Information provided to DPR during the preparation of this report indicates the potential of an inversion during the period of the application. The presence of an inversion would be inconsistent with current requirements. However, the ability to determine whether an inversion was present during the application cannot

be made. Given this uncertainty, caution should be taken with respect to the air concentrations and other values calculated from the study. Even so, because sprinkler applications are still allowed at night, this study appears to be representative of current practices (Barry and Johnson, 2001).

The study on off-site air movement of MITC from the application of metam-sodium through shank injection and sprinkler irrigation (MSTF, 1999b) was flawed because results indicated that not all sampling stations were located in the downwind direction. The exposure of residents to MITC from this study is likely underestimated. Furthermore, results of field fortification recoveries ranged from 44 to 3,486% for the study using sprinkler irrigation application. The report revealed that upwind air samples for two of the sites appeared to be contaminated with MITC. This caused some uncertainty on the adjustment of MITC concentrations. To correct for these deficiencies, the MSTF should conduct or sponsor a study so that representative MITC concentrations can be obtained.

Exposure estimates for some studies contained in this document are shown as absorbed dosages of MITC for adult male workers, male and female adult residents, and children. The absorbed dosages were determined as an absorbed daily dosage (ADD), a seasonal average daily dosage (SADD), and an annual average daily dosage (AADD). These absorbed dosages were previously employed in the risk assessment of MITC because the toxicological endpoints used for the calculation of the margin of exposure (MOE) were determined as absorbed dosages. Later in the risk assessment process, the risk assessor changed the toxicological endpoints from using absorbed dosages to air concentrations. The risk assessor simply calculated MITC air concentrations from the absorbed dosages contained in the previous version of exposure document. For subsequent studies, exposures for agricultural workers are shown as 1-hour, 8-hour, intermediate-term, and long-term MITC concentrations and those for residents (adult males and females, and children) are shown as 1-hour, 8-hour, 24-hour, intermediate-term, and long-term MITC concentrations instead of absorbed dosages.

For this current revision, previously determined MITC absorbed dosages are retained in this document so as to save staff time for both the risk and exposure assessors. Otherwise, the assessors have to spend more time revising the exposure and risk characterization documents.

Exposure data were adjusted to reflect field fortification recoveries and the maximum metam-sodium application (label) rate of 318 lbs AI per acre, unless noted otherwise. Half of the minimum detection limit (MDL) or limit of quantitation (LOQ) was used when the report indicated residues were nondetectable (ND), unless mentioned otherwise in this document.

Several default factors are needed for the calculation of MITC exposures for workers and residents. These principal default factors are listed in Table 6 and below.

Table 6. Factors employed in the calculation of exposures of workers and residents to MITC.

| Exposure | Person | BW (kg) | Inhalation rate | Exposure days | Reference |
|---|---|---|---|---|---|
| A. Workers | | | | | |
| Short-term | Adult male | 77 | 0.84 $m^3$/h | Daily | U.S. EPA, 1997 (T. 7-4, 5-14) |
| Short-term | Adult female | 62 | 0.66 $m^3$/h | Daily | U.S. EPA, 1997 (T. 7-5, 5-14) |
| Int.-term | Adult male | 77 | 0.84 $m^3$/h | 23/120[a] | U.S. EPA, 1997 (T. 7-4, 5-14) |
| Int.-term | Adult female | 62 | 0.66 $m^3$/h | 23/120[a] | U.S. EPA, 1997 (T. 7-5, 5-14) |
| Long-term | Adult male | 77 | 0.84 $m^3$/h | 70/365[a] | U.S. EPA, 1997 (T. 7-4, 5-14) |
| Long-term | Adult female | 62 | 0.66 $m^3$/h | 70/365[a] | U.S. EPA, 1997 (T. 7-5, 5-14) |
| B. Residents (adults) | | | | | |
| Short-term | Adult male | 77 | 21.4 $m^3$/day | Daily | U.S. EPA, 1997 (T. 7-4, 5-18) |
| Short-term | Adult female | 62 | 11.8 $m^3$/day | Daily | U.S. EPA, 1997 (T. 7-5, 5-18) |
| Int.-term | Adult male | 77 | 21.4 $m^3$/day | 23/120[a,b] | U.S. EPA, 1997 (T. 7-4, 5-18) |
| Int.-term | Adult female | 62 | 11.8 $m^3$/day | 23/120[a,b] | U.S. EPA, 1997 (T. 7-4, 5-18) |
| Long-term | Adult male | 77 | 21.4 $m^3$/day | 70/365[a,b] | U.S. EPA, 1997 (T. 7-4, 5-18) |
| Long-term | Adult female | 62 | 11.8 $m^3$/day | 70/365[a,b] | U.S. EPA, 1997 (T. 7-4, 5-18) |
| C. Residents (children) | | | | | |
| Short-term | Children | 22[c] | 16.74 $m^3$/day[c] | Daily | U.S. EPA, 1997 (T. 7-6, 5-18) |
| Int.-term | Children | 22[c] | 16.74 $m^3$/day[c] | 23/120[a,b] | U.S. EPA, 1997 (T. 7-6, 5-18) |
| Long-term | Children | 22[c] | 16.74 $m^3$/day[c] | 70/365[a,b] | U.S. EPA, 1997 (T. 7-6, 5-18) |

[a] For intermediate (Int.)- and long-term exposure, frequency of exposure is 23 days in a 120-day period equivalent to 70 exposure days in 365 days, except for exposure of residents to MITC in ambient air (See[b] below). The exposure days are applicable to workers who are exposed to MITC while performing handling activities, and residents who are exposed to MITC in the vicinity of treated fields (from application site monitoring). The number of workdays or exposure days per season (23/120) was based on data from Haskell (1994). Handlers (pest control operators) were assumed to work 15 days for a 12-hour shift, equivalent to 23 days for an 8-hour shift in a 120-day season (or proportional to 17.25 days in a 90-day period). Residents were assumed to be exposed to airborne MITC from fumigated fields at the same number of days (23 days) in a 120-day season. This is based on the assumption that wind would not blow from treated fields to a residential area in the same direction all the time and agricultural areas in the same vicinity would not be fumigated continuously longer than 23 days in a 120-day season.

[b] Average frequency of exposure of residents to ambient MITC (ambient monitoring studies for studies B.2, B.7, and B.9) is 78 days in a 90-day period and 188 days per year (365 days) (Powell, 1999).

[c] Body weight and inhalation rate for six-year-old children. Based on available information, the ratio of inhalation rates and body weights of six-year-old male children is the highest for resting, light, and moderate activities (U.S. EPA, 1997).

Calculation procedures and some default factors

1. MITC: air concentration ($\mu g/m^3$) = [(correction factor) x MW x (ppb)]/24.45
   or $\mu g/m^3$ = adjusted ppb x 2.99; ppb = adjusted $\mu g/m^3$ x 0.334. (MITC MW = 73.1)
   Where correction factor = [(318 lbs AI/acre (max.)]/[appl. rate (lbs AI/acre)] x [% observed recovery]$^{-1}$
   (Note: One gram mole of an ideal gas or vapor occupies a volume of 24.45 liters at 25 $^{o}$C and 760 mmHg pressure.)

2. Short-term exposure:
   ADD ($\mu g$/kg body weight/day) = [$\mu g/m^3$ (use short-term air concentration) x inhalation rate ($m^3$/h or $m^3$/day)]/[BW]

3. Intermediate-term exposure:
   SADD ($\mu g$/kg body weight/day) = $\frac{\text{ADD (for SADD calculation) x Exposure days in a time period or season}}{\text{Days in a time period or season}}$
   Use intermediate-term air concentrations residential exposure and daily inhalation rates. These inhalation rates take into account the activity patterns in respect to resting, light, moderate, and heavy activities.

4. Long-term exposure:
   AADD ($\mu g$/kg body weight/day) = $\frac{\text{ADD (for AADD calculation) x Exposure days in a year}}{\text{365 days/year}}$

   Use long-term air concentrations for residential exposure and daily inhalation rates. These inhalation rates take into account the activity patterns in respect to resting, light, moderate, and heavy activities.

5. Assume applicators, loader/applicators, and monitors work 8 hours/day. The work times for loaders are based on proportion of average work times for loaders and applicators from the submitted reports. The work times for loaders are 49 min. for rotary tiller injection, 16 min. for center-pivot sprinkler irrigation, 51 min. for shank injection, 124 min. for solid-set sprinkler irrigation, and 8 hours for loaders/applicators of drip irrigation application.

An example of exposure calculation is shown in Table 7.

Table 7. Example of MITC exposure calculation for adult male workers[a] (Air monitoring in Kern County, CARB, 1997).

| Downwind sample ID | | Time (min) | MITC (ppb) | Appln. rate (lb AI/A) | Adjusted for appln. rate (ppb) | Recovery (%) | Adjusted for recovery (ppb) | µg/m$^3$ | TWA[b] µg/m$^3$ | Inhalation rate (m$^3$/day) | Exposure (µg/day) | ADD (µg/kg/day) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NC | For ADD[c] | 760 | 84 | 155 | 172 | 73 | 236 | 707 | N/A | 21.4 | 15,126 | 196.4 |
| NC | For SADD[d] | 370 | 0.21 | 155 | 0.43 | 73 | 0.59 | 1.77 | | | | |
| | Or AADD[e] | 760 | 84 | 155 | 172 | 73 | 236 | 707 | | | | |
| | | 675 | 2.7 | 155 | 5.54 | 73 | 7.59 | 22.7 | | | | |
| | | 770 | 57 | 155 | 117 | 73 | 160 | 480 | 245 | 21.4 | 5,244 | 68.1 |
| | | 600 | 1.1 | 155 | 2.26 | 73 | 3.09 | 9.26 | | | | |
| | | 795 | 6.7 | 155 | 13.8 | 73 | 18.8 | 56.4 | | | | |

| TWA µg/m$^3$ | Inhalation rate (m$^3$/day) | Exposure (µg/day) | ADD (µg/kg/day) | SADD (µg/kg/day) |
|---|---|---|---|---|
| 245 | 21.4 | 5,244 | 68.1 | 13.05 |

| TWA µg/m$^3$ | Inhalation rate (m$^3$/day) | Exposure (µg/day) | ADD (µg/kg/day) | AADD (µg/kg/day) |
|---|---|---|---|---|
| 245 | 21.4 | 5,244 | 68.1 | 13.05 |

Appln. is application.

[a] Physiologic factors used to calculate exposure for adult males are: body weight = 77 kg and inhalation rate = 0.84 m$^3$/h.

[b] TWA (time-weighted average) = $(C_1T_1 + C_2T_2 + .....C_nT_n)/(T_1 + T_2 + .....T_n)$. $C_1$ is MITC concentration at time $T_1$, $C_n$ is MITC concentration at time $T_n$.

[c] ADD (absorbed daily dosage, µg/kg body weight/day) = [µg/m$^3$ (use short-term air concentration) x inhalation rate (m$^3$/h or m$^3$/day)]/[BW].

[d] SADD (seasonal average daily dosage, µg/kg body weight/day) = $\frac{\text{ADD (for SADD calculation) x Exposure days in a time period or season}}{\text{Days in a time period or season}}$

[e] AADD (annual average daily dosage, µg/kg body weight/day) = $\frac{\text{ADD (for AADD calculation) x Exposure days in a year}}{\text{365 days/year}}$

Results: ADD = 196.4 µg MITC/kg body weight/day; SADD = 13.05 µg MITC/kg body weight/day; AADD = 13.05 µg MITC/kg body weight/day.

Determination of short-term (1- and 8-hour) MITC air concentrations for handlers and residents
Short-term MITC air concentrations are estimated for 1- and 8-hour exposure periods by using data obtained from some of the studies shown in this document. Short-term exposures of 1 or 8 hours for handlers and 1, 8, and 24 hours for residents are intended for use in the risk assessment of MITC for acute effects because the acute NOEL values for MITC relate directly only to 1-, 8-, or 24-hour exposures.

The sampling times used in the above-mentioned studies for workers ranged from 3 minutes to 254 minutes. Sampling times for off-site and ambient MITC monitoring studies ranged from 1 to 24 hours. In order to estimate 1- and 8-hour MITC air concentrations for risk assessment, the following assumptions (Table 8) are necessary and used whenever they are applicable.

Table 8. Determination of short-term (1- & 8-hour) MITC concentrations for handlers and residents.

| Sampling period | 1-hour MITC concentrations | 8-hour MITC concentrations |
|---|---|---|
| 1. Short sampling time, e.g., 3 to 25 minutes. | Use the average MITC air concentration for that work task or exposure scenario. | Use the average MITC air concentration for that work task or exposure scenario. |
| 2. Moderate sampling time, e.g., 1 to 9 hours. | Use the highest MITC air concentration from a replicate of that work task or exposure scenario. | Use the average MITC concentration if the sampling time is shorter than 5 hours or calculate the 8-hour TWA for the sampling time of 8 hours or closest to 8 hours. |
| 3. Long sampling time, e.g., 10 to 24 hours. (For residents) | Use the highest MITC air concentration from a replicate of that work task or exposure scenario. | Use the highest MITC air concentration from a replicate of that work task or exposure scenario. |

An attempt was made to estimate days of exposure of metam-sodium applicators to MITC in four highest use counties (Fresno, Kern, Santa Barbara, and Stanislaus) based on the pesticide use report. The approach used to estimate frequency of exposure for residents could not be used to estimate days of exposure for metam-sodium applicators because there was some difficulty in obtaining the accurate number of applicators in those counties. Bergeson suggested eight days of exposure per season or year for workers and residents (Bergeson, 1999). However, Bergeson did not provide adequate background information to substantiate how the suggested days of exposure were obtained. However, a report prepared by Sullivan (2002) indicated that a custom shank applicator may work up to 200 days per year.

**A. Exposure of handlers or pest control operators to MITC**
Four worker exposure studies were submitted to DPR for consideration. The first study was conducted in Yuma, Arizona in 1992 (ICI Americas Inc., 1992). The second study was conducted in Grant County, Washington in 1993 (Zeneca Inc., 1993a), the third study was conducted in Kern County, California in 1999 (MSTF, 1999a), and the fourth study was performed in Kern County in 2000 (MSTF, 2001). Locations of the test sites in Arizona and Washington represented two different climatic conditions. The test site in Arizona represented dry and warm areas; whereas, the test site in Washington represented cool and wet areas. The

test site in California represented dry and warm area similar to the test site in Arizona. All studies were conducted in accordance with U.S. EPA Good Laboratory Practice Standards (40 CFR, Part 160). Studies conducted by ICI Americas (1992) and Zeneca (1993a) are retained in this document to provide historical perspective, only.

A.1 Worker exposure study in Arizona (Retained for historical perspective only)

Shank injection

Metam-sodium (Busan 1020®, 32.7%; 3.18 lbs AI/gallon) was applied at the maximum label rate of 100 gallons per acre (318 lbs AI/acre). Two tractors, a John Deere 4455 equipped with an enclosed-cab and air conditioning, and John Deere 4430 equipped with an open-cab, were used to pull the shank injection rig. The closed cab was equipped with a charcoal air filter during the first two replicates and a standard cellulose air filter for replicates three to six. Application of metam-sodium was conducted in disced fields. Replicates seven to ten were conducted using the open-cab tractor. Ten loader and ten applicator replicates were conducted in this study. Four male volunteers were monitored during the shank injection. The length of each loader replicate represented the time period to load a minimum of 100 gallons of Busan 1020®, which ranged from 3 to 17 minutes. Application replicates ranged from 60 to 78 minutes. During the study, each worker wore long-sleeved shirts, long pants, underwear, and socks. In addition, the loaders wore rubber boots, goggles, chemical-resistant gloves, and respirators. Applicators were provided with goggles, chemical-resistant gloves, and respirators to wear at their own discretion or when a pungent, rotten-egg odor was detected.

Duties of a loader included attaching one end of a hose to a fitting on the shank-application tank. He then opened the seal on the tanker, screwed the coupler into place, and attached the other end of the hose to the coupler. He opened a valve on the tanker, allowing metam-sodium to flow into the application tank. When the tank was full, he closed the valves at the tanker and application tank and uncoupled the hose from the application tank. During this work activity, some metam-sodium remaining in the hose would spill onto his gloves and the ground. While the application tank was filling up with metam-sodium, the loader sat either on the tool bar of the injector or on the back of the tanker trailer.

The shank injection rig had a 200-gallon tank secured above three tool bars. The applicator stayed in the cab during the whole application replicate unless he performed maintenance work on the tractor or shank. Metam-sodium was applied when the shanks were fully inserted in the ground and shut off when the shanks were lifted from the ground.

Solid-set sprinkler irrigation

Metam-sodium (Busan 1020®, 32.7%; 3.18 lbs AI/gallon) was applied at the maximum label rate of 100 gallons per acre (318 lbs AI/acre). Application of metam-sodium was conducted in disced fields. Ten loader and ten applicator replicates were conducted in this study. The sprinkler trial used a total of five male volunteers (three loaders and two applicators). The length of each loader replicate represented the time period to load a minimum of 100 gallons of Busan 1020®, which ranged from 43 to 78 minutes. Application replicates ranged from 240 (4 hours) to 254 minutes (4.23 hours).

During the study each worker wore long-sleeved shirts, long pants, underwear, and socks. In addition, the loaders wore rubber boots, goggles, chemical-resistant gloves, and respirators. Applicators were provided with goggles, chemical-resistant gloves and respirators to wear at their own discretion or when a pungent, rotten-egg odor was detected.

For a typical sprinkler irrigation application, a loader attached one end of a hose to a coupler on the tanker. The other end was dropped through an opening of the 200-gallon holding tank located in the bed of a pickup truck. The loader then opened the valve on the tanker, allowing the metam-sodium to fill the tank. When the tank was filled, he closed the valve on the tanker and pulled the hose out of the holding tank. The loader drove the pickup truck to the nurse tank and transferred metam-sodium to the nurse tank using a hose. During the transferring procedure, some metam-sodium remaining in the hose would drip onto the gloves and onto the ground. While the nurse tank was being filled with metam-sodium, the loader would sit on the back of the tanker truck.

There were a total of 32 sprinkler lines in the field with 42 sprinkler heads per line. Each metal sprinkler line measured 1,260 feet. At the beginning of each replicate, the applicator walked into the field and manually turned on the three new sprinkler lines and closed off the previous three. During this period, only water was running. The applicator then walked down the field to check the conditions of sprinkler heads. Even though, metam-sodium was not applied at this time, the applicator could detect the odor from the previous application. The applicator usually wore protective clothing during the inspection procedure. After watering, which lasted for 30 minutes, the applicator turned on the injector pump that pumped metam-sodium from the nurse tank into the sprinkler line, opened a valve to release the metam-sodium from the nurse tank, and opened the valve to the main irrigation line. It took about two hours to apply the 345 gallons metam-sodium during each replicate. During the application, the applicator checked the flow rate of metam-sodium about every half hour and occasionally checked irrigation pumps and water levels in the irrigation canal. When the application was done, the applicator turned off the injection pump and closed the two valves. Water was continuously applied to the field for about 1.5 hours after metam-sodium application.

Inhalation exposure monitoring

Inhalation exposure to MITC was monitored using charcoal vapor-collection tubes (400/200 mg, SKC Cat. N0. 226-09). A glass fiber filter and a silica gel drying tube were placed in front of each charcoal vapor-collection tube. The drying tube was used to trap moisture. Each worker wore a personal air sampling pump (MSA Model S, G, or Flow-Lite H or SKC Model 224-43XR) on his belt. Air was drawn from the worker's breathing zone at a set flow rate of 1 L/min. Only charcoal vapor-collection tubes (not the moisture traps) were collected and stored on dry ice for analysis.

The field fortification recovery study was performed using the same method employed in the study conducted in Washington.

Analysis and recovery

MITC was analyzed using the slightly modified Method No. RRC-82-35, supplied by Zeneca Inc. (1993a). Both methods were validated prior to study commencement. The minimum quantitative limit (MQL) for MITC was 1.0 µg per sample section. In the report, MITC levels were calculated using the MQL value when residue levels were less than MQL. Typically, staff of the Exposure Assessment and Mitigation Group of WH&S uses ½ MQL or ½ MDL for the estimation of worker exposure when residues are not detected. Therefore, when the report indicated non-detects for the front and rear sections of the sampling train, a total of 1.0 µg, instead of 2.0 µg, is used for that sample. MITC residues were adjusted for field fortification recoveries, averaging 84.3% for shank injection and 94.8% for sprinkler injection. These recovery studies were conducted during exposure studies using the two application methods in different dates. Air concentrations of MITC are shown in Table 9. Absorbed dosages shown in Table 10 represent the exposure estimates for adult male workers. MITC concentrations for 1- and 8-hour exposures were determined based on criteria shown in Table 8 and the results are shown in Table 16.

Table 9. Air concentrations of MITC during loading and soil application of metam-sodium using shanks, solid-set sprinklers, rotary tillers, and center-pivot sprinklers.

| Study | Work task | Air concentrations of MITC (ppb)[a] n[b] | Mean | SD[b] | Range |
|---|---|---|---|---|---|
| ***A.1 Arizona (warm and dry)***[c] (Retained for historical perspective only) | | | | | |
| Shank injection | Loader | 10 | 134 | 129 | 10.6-387 |
| | Applicator[d] | 2 | 76.5 | 26.3 | 57.9-95.1 |
| | Applicator[e] | 4 | 504 | 92.4 | 378-600 |
| | Applicator[f] | 4 | 437 | 573 | 74.1-1291 |
| Solid-set sprinklers | Loader | 10 | 288 | 322 | 25.8-914 |
| | Applicator | 10 | 500 | 374 | 27.5-954 |
| ***A.2 Washington (cool and wet)***[c] (Retained for historical perspective only) | | | | | |
| Rotary tiller | Loader | 10 | 152 | 175 | 30.4-553 |
| | Applicator[d] | 5 | 284 | 311 | 78.8-832 |
| | Applicator[e] | 5 | 224 | 141 | 69.9-405 |
| Center-pivot sprinklers | Loader | 5 | 34.5 | 6.09 | 27.9-41.8 |
| | Applicator | 5 | 29.3 | 7.63 | 23.8-42.4 |

[a] Air concentrations were adjusted for field fortification recoveries, but not for the maximum label rate since the application rates used in the studies were similar to the maximum label rate.

[b] n is number of replicates, SD is standard deviation.

[c] Exposure data obtained from the study may represent extreme case exposure scenarios because the application procedures, as recommended in the TIB have improved in recent years. The study was included in this document to provide historical perspective.

[d] Closed cab with a charcoal air filter.

[e] Closed cab with a cellulose air filter.

[f] Open cab.

A.2 Worker exposure study in Washington (Retained for historical perspective only)

Rotary tiller injection

Metam-sodium (Vapam® 32.7%; 3.18 lbs AI/gallon) was scheduled to be applied at the maximum label rate of 100 gallons per acre (318 lbs AI/acre). However, the actual application rate averaged 320 lbs AI/acre. About 10 acres of disced field was used for the injection trial for the first four replicates. Replicates 5 through 10 were conducted in about 65 acres of disced field.

Ten loader and ten applicator replicates were conducted for the rotary tiller injection method. Three male volunteers were monitored during the application of metam-sodium. The length of each loader replicate represented the time period to load a minimum of 100 gallons of metam-sodium (Vapam®) that ranged from 3 to 11 minutes. The time period for application replicates ranged from 56 to 72 minutes. Both the loaders and applicators wore long-sleeved shirts and long pants during the study. In addition, loaders wore rubber boots, goggles, chemical-resistant gloves, and respirators. Applicators were provided with goggles, chemical-resistant gloves, and respirators to wear at their own discretion or when a pungent, rotten-egg odor was detected.

All replicates were conducted using an enclosed cab tractor equipped with an air conditioning and air-filtering unit. The cab was equipped with a charcoal air filter during the first five replicates and a cellulose air filter for replicates six through ten. This tractor was used to pull the rotary injection rig. The rotary tiller had a 220-gallon tank secured above the tool bar. A large roller was attached behind the tool bar to seal the soil after injection.

Duties of a loader included connecting a hose to the application tank and opening and closing valves. When the work was done, the loader disconnected the hose, removed it from the tank, and placed it on the ground. While the application tank was filling up with metam-sodium, the loader sat either on the tool bar of the injector or on the back of the tanker trailer.

The applicator stayed in the cab during the whole application replicate, unless he performed maintenance work on the tractor. Metam-sodium was applied when the blades were fully in the ground and shut off when the blades were lifted from the ground.

Center-pivot sprinkler irrigation

Metam-sodium (Vapam® 32.7%; 3.18 lbs AI/gallon) was scheduled to be applied at the maximum label rate of 100 gallons per acre (318 lbs AI/acre). However, the actual application rate averaged 290 lbs AI/acre. The application site was a 145-acre field of dormant alfalfa.

The sprinkler irrigation system was a full-sized center pivot with 72-low angle impact nozzles. Metam-sodium was injected into the system at the center pivot. Water, with a pH of 6, was supplied from a nearby well. The 1,266-foot boom was constructed with 6-inch galvanized overhead spans. These nozzles were located approximately 14 feet above the ground. The tank capacity was approximately 3,800 gallons. The injector pump was a John Blue High Capacity piston pump.

For a typical sprinkler irrigation application, a loader attached one end of a hose to a coupler on the tanker. The other end was dropped through an opening of a nurse tank located next to the center pivot and secured with a wire. The loader then opened the valve on the tanker, allowing the metam-sodium to fill the nurse tank. When the tank was filled, he closed the valve on the tanker and pulled the hose from the nurse tank and placed it on the ground. The applicator walked to the injector pump every half hour to check the injection flow rate. When the nurse tank was nearly empty, the applicator flipped a lever to close the line and another lever to open the next tank. For most of the time during each replicate, the applicator sat in his car parked 10 to 50 feet from the center pivot.

Five loader and five applicator replicates were conducted for the sprinkler irrigation method. Three male volunteers were monitored during the application of metam-sodium. The length of loader replicates ranged from 8 to 12 minutes, corresponding to loading 598 to 769 gallons of metam-sodium (Vapam®). The time period for application replicates ranged from 224 (3.73 hours) to 241 minutes (4.0 hours). Both loaders and applicators wore long-sleeved shirts and long pants during the study. In addition, loaders wore rubber boots, goggles, chemical-resistant gloves and respirators. Applicators were provided with goggles, chemical-resistant gloves and respirators to wear at their own discretion or when a pungent, rotten-egg odor was detected.

Inhalation exposure monitoring

Inhalation exposure to MITC was monitored using charcoal vapor-collection tubes (400/200 mg, SKC Cat. No. 226-09). A glass fiber filter and a silica gel drying tube were placed in front of each charcoal vapor-collection tube. The glass fiber filter was used to trap dust particles and the silica gel drying tube was used to trap moisture. Each worker wore an air-sampling pump (MSA Model S, G, or Flow-Lite H or SKC Model 224-43XR) on his belt. Air was drawn from the worker's breathing zone at a set flow rate of 1 L/min. Only the charcoal vapor-collection tubes (not the moisture traps) were collected and stored on dry ice for analysis.

Silica gel drying tubes were also used in subsequent studies employed in this exposure document. MITC in silica gel portion of the sampling train was not analyzed, except for a study conducted by Wofford *et al*. (1994). In this study, silica gel tubes were found to retain MITC ranging from 58 to 100% for one sampling interval and 0 to 4% for another sampling interval. It appeared that retention of MITC in silica gel drying tubes is not consistent. However, there are concerns about the MITC absorption efficiency of silica gel drying tubes. These drying tubes were recommended in the standard operating procedure of registrants. There is a possibility that those data obtained without analyzing drying tubes for MITC may underestimate exposures. However, results of a field fortification study showed recoveries were greater than 86%, and that from studies in two days conducted by Zeneca Inc. (1993b) averaged 97.8% and 100%.

Field fortification of the charcoal vapor-collection tubes was conducted for MITC at 1,000, 100 and 1 μg. After the charcoal tubes were fortified directly with MITC reference standard (liquid), a glass fiber filter and a silica gel drying tube were placed in front of each chemical collection tube. The glass fiber filter was used to trap dust particles and the drying tube was used to trap moisture. This field fortification method bypasses the drying tubes and thus does not indicate the MITC retention in the drying tubes. Air was drawn through various tubes at the rate of 1.0 L/min

for the same duration as that for inhalation exposure monitoring. Air pumps were located at the upwind area away from the test site. Control samples were also setup similarly to that of the field fortification samples and operated concurrently with field fortification samples, except there was no fortification with MITC.

Analysis and recovery

MITC was analyzed using the slightly modified Method No. RRC-82-35, supplied by Zeneca Inc. (1993a). The method was validated prior to study commencement. The MQL for MITC was 1.0 μg per sample section. MITC levels in the submitted report were calculated using the MQL whenever residue levels were less than the MQL. Typically, staff of the Exposure Assessment and Mitigation Group of WH&S uses ½ MQL or ½ MDL for the estimation of worker exposure when residues are not detected. Therefore, when the report indicated non-detects for the front and rear sections of the sampling train, a total of 1.0 μg, instead of 2.0 μg, is used for that sample. MITC residues, as presented in the submitted documents, were adjusted according to recoveries of field fortification samples for a given day. The average recoveries were 86.8% during the study using rotary tiller injection and 88.3% during the study using sprinkler irrigation. Air concentrations of MITC are shown in Table 9. Absorbed dosages shown in Table 10 represent the exposure estimates for adult male workers. MITC concentrations for 1- and 8-hour exposures were determined based on criteria shown in Table 8 and the results are shown in Table 16.

Table 10. Exposure of adult male workers to MITC during loading and application of metam-sodium using shanks, solid-set sprinklers, rotary tillers, and center-pivot sprinklers.

| | | | Average dosages of MITC (μg/kg/day)[a] | | |
|---|---|---|---|---|---|
| | | | ADD[b] | SADD[c] | AADD[d] |
| | Work task | n | Mean ± SD (Range) | Mean ± SD (Range) | Mean ± SD (Range) |
| ***A.1 Arizona (warm and dry)***[e] (Retained for historical perspective only) | | | | | |
| Shank injection | Loader | 10 | 3.70 ± 3.57 (0.29-10.7) | 0.71 ± 0.68 (0.06-2.05) | 0.71 ± 0.68 (0.06-2.05) |
| | Applicator[f] | 2 | 20.0 ± 6.86 (15.1-24.8) | 3.83 ± 1.32 (2.90-4.76) | 3.83 ± 1.32 (2.90-4.76) |
| | Applicator[g] | 4 | 132 ± 24.2 (98.8-157) | 25.3 ± 4.63 (18.9-30.1) | 25.3 ± 4.63 (18.9-30.1) |
| | Applicator[h] | 4 | 114 ±150 (19.4-337) | 21.9 ± 28.7 (3.71-64.6) | 21.9 ± 28.7 (3.71-64.6) |
| Solid-set sprinkler | Loader | 10 | 19.5 ± 21.8 (1.75-61.9) | 3.73 ± 4.18 (0.34-11.9) | 3.73 ± 4.18 (0.34-11.9) |
| | Applicator | 10 | 131 ± 97.7 (7.18-249) | 25.0 ± 18.7 (1.38-47.8) | 25.0 ± 18.7 (1.38-47.8) |
| ***A.2 Washington (cool and wet)***[e] (Retained for historical perspective only) | | | | | |
| Rotary tiller | Loader | 10 | 4.08 ± 4.71 (0.82-14.8) | 0.78 ± 0.90 (0.16-2.84) | 0.78 ± 0.90 (0.16-2.84) |
| | Applicator[f] | 5 | 74.2 ± 81.2 (20.6-217) | 14.2 ± 15.6 (3.95-41.7) | 14.2 ± 15.6 (3.95-41.7) |
| | Applicator[g] | 5 | 58.5 ± 36.9 (18.3-105) | 11.2 ± 7.08 (3.50-20.3) | 11.2 ± 7.08 (3.50-20.3) |
| Center-pivot sprinkler | Loader | 5 | 0.30 ± 0.05 (0.24-0.36) | 0.06 ± 0.01 (0.05-0.07) | 0.06 ± 0.01 (0.05-0.07) |
| | Applicator | 5 | 7.65 ± 1.99 (6.23-11.1) | 1.47 ± 0.38 (1.19-2.12) | 1.47 ± 0.38 (1.19-2.12) |

[a] The average dosage of an adult female is 0.98 times that of an adult male. The exposure ratio (inhalation rate ÷ BW) for females and males = ((0.66 $m^3$/h ÷ 62 kg) ÷ (0.84 $m^3$/h ÷ 77 kg)) = 0.98) (Table 6 or U.S. EPA, 1997). MITC concentrations were calculated based on a maximum labeling rate of 75 gallons/acre. For shank injection, the exposure estimates are reduced 50% if metam-sodium is applied to planting beds at an application rate of 37.5 gallons/acre or 75 gallons/treated acre.

[b] ADD (absorbed daily dosage, μg/kg body weight/day) = [μg/$m^3$ (use short-term air concentration) x inhalation rate ($m^3$/h or $m^3$/day)]/[BW].

[c] SADD (seasonal average daily dosage, μg/kg body weight/day) = $\frac{\text{ADD x Exposure days in a time period or season}}{\text{Days in a time period or season}}$

SADD was calculated based on 23 workdays in a 120-day season.

[d] AADD (annual average daily dosage, μg/kg body weight/day) = $\frac{\text{ADD x Exposure days in a year}}{\text{365 days/year}}$

AADD was calculated based on 70 workdays in a year (or 23 workdays x 365 days per year/120 workdays per season).

[e] Exposure data obtained from the study may represent extreme case exposure scenarios because the application procedures, as recommended in the TIB have improved in recent years. The study was included in this document to provide historical perspective.

[f] Closed cab with a charcoal filter.

[g] Closed cab with a cellulose air filter.

[h] Open cab.

A.3 Determination of methyl isothiocyanate inhalation exposure to workers as they apply metam-sodium through shank injection and sprinkler irrigation

In June 1999, Agrisearch Incorporated conducted a study sponsored by the MSTF and Bergeson and Campbell to determine MITC inhalation exposure to workers as they applied metam-sodium through shank injection and sprinkler irrigation (MSTF, 1999a). This study was conducted based upon the U.S. EPA OPPTS Harmonized Series 875, "Occupational and Residential Exposure Test Guidelines." The Department of Pesticide Regulation in cooperation with the Committee on Human Research of the University of California, San Francisco reviewed and approved the study protocol and consent form (Approval number H7420-16288-01, May 27, 1999). Metam-sodium was applied according to the recommendations of the TIB (February 1999). Two carrot growing fields located in Bakersfield, Kern County were used in the study.

Sprinkler irrigation

The sprinkler irrigation method was employed to apply metam-sodium at a rate of 75-gallon formulation (VAPAM® HL, 42% AI, 4.26 lbs of metam-sodium per gallon) per acre (319.5 lbs AI/acre) to about 80 acres of a carrot field (site 1). This field was divided into four application plots, approximately 20 acres per plot. A main water line ran down the middle of the application plots east to west. The irrigation pipe attached to the main water line was placed north to south on 12.2 m (40 ft.) centers. Sprinkler heads were located every 9.1 m (30 ft.) along irrigation pipes throughout the application plots.

Metam-sodium was injected into the water flowing from the well to the sprinkler lines. The metam-sodium contained in the farm tank was delivered to a 4-hp pump and to the main water line through a 1-inch diameter neoprene line. The injection rate was 250 gallons per hour. The total application time for 1,500 gallons of metam-sodium per 20-acre plot was 6 hours. Approximately 1½ acre-inch water was irrigated onto the field to apply 75 gallons of metam-sodium per acre. The sprinkler irrigation was performed over a four-day period based on the application of 20 acres/day.

Shank injection

The shank injection method was used to apply metam-sodium to an approximately 80-acre bare ground field (site 2) at a rate of 75 gallons of formulation (VAPAM® HL) per treated acre (319.5 lbs AI/acre). The application plot was set the same as site 1 except the main water line was disconnected at each irrigation pipe and laid against irrigation pipe to allow for shank injection. Metam-sodium was transferred from the farm tank to the tank on the shank unit by using a transfer pump followed by water to flush lines and load enough water to apply approximately 37.5 gallons of formulation (159.75 lbs AI/acre) plus 25 gallons of water per acre. The shank equipment applied metam-sodium only in the bed area and not between beds. Therefore, the application rate was approximately 37.5 gallons per acre. The shank injection application employed two injection rigs operating between every other pair of irrigation pipes. As the shank injection unit passed through the field, soil was formed as a planting bed approximately 10 inches deep (as a final soil cap). The application was completed in one day. As the treatment progressed, the irrigation crew reconnected the main irrigation pipe and the first 1/3 of the field

was irrigated for 2 hours. Thereafter, the middle and last plots were each irrigated for about 2.5 hours. This provides a ½ inch water cap to the field post application and a soil cap.

Odor control

The odor control measures for sprinkler irrigation as required by the product label and the TIB included:

- pre-application irrigation.
- applied when air temperature <90 $^{o}$F and wind speed was ≤7 mph.
- applied when there was no thermal inversion near or at the ground.
- applied ½ inch water cap immediately post application.
- applied an additional ½ inch water cap within 24 hours post application.

The odor control measures for shank injection as required by the product label and the TIB included:

- pre-application irrigation.
- applied when soil temperature <90 $^{o}$F.
- created soil cap at application.
- applied ½ inch water cap immediately post application.

Sample collection

The charcoal-vapor collection tube (400/200 mg, SKC Cat. No. 226-09) was used to sample MITC concentrations in the breathing zone of workers as they monitored the sprinkler irrigation, applied metam-sodium by shank injection or applied a water cap at the shank injection site by sprinkler irrigation. A personal air-sampling pump (Gilian Model HFS 113A) was attached to the belt around the waist of the worker. Tygon® tubing attached to the inlet valve of the pump was placed over the shoulder of the worker and attached to the sorbent tube. A clip was used to attach the charcoal sorbent tube to the collar, thus positioning it in the worker's breathing zone. During shank injection, an additional sampling pump and charcoal tube was operated in the cab of the tractor with the charcoal tube near the breathing zone of the applicator. This sorbent tube measured application exposure for an applicator who did not leave the cab. The flow rate of the pump was approximately 1 liter/min. The samples were stored frozen and shipped frozen on dry ice. The samples were stored frozen at the lab for up to 9 days at –9 $^{o}$C to 6 $^{o}$C.

Field fortification recovery

Before the study initiation, the limit of quantitation (LOQ) was determined to be 0.1 µg per sorbent tube or tube section. Also, Agrisearch determined that a silica gel prefilter for moisture was not required because the method try out suggested that the MITC extraction efficiency from charcoal using 20% $CS_2$ in ethyl acetate was greater after high humidity weathering of fortified tubes than after dry weathering of tubes. This means that moisture in the air during the study does not alter MITC extraction efficiency.

A field recovery study of fortified samples was conducted. Sorbent tubes were spiked with aliquots of the fortification solution, which was supplied by the analytical laboratory, at 0.5 µg and 10 µg. Three replicate samples at the two rates were fortified at each site on each date. The

air sampling system was located upwind of the treated field and was run at 1.0 L/min. However, upwind air samples for two of the sites appeared to be contaminated with MITC. Results of the studies revealed that the highest MITC air concentrations were not observed at the same sampling site. This led to the conclusion that the wind directions changed during the study periods. Results of field fortification recoveries ranged from 44 to 3,486% for the sprinkler irrigation study. However, the average recovery was 86 ± 7% (range 74-99%) after the background MITC, which was found in control samples, was subtracted from fortified samples that showed very high recoveries. MITC concentrations were adjusted for the average recovery of 86%. The average field fortification recovery during the shank injection study was 99 ± 13% (range 81-117%). MITC concentrations obtained from the study using shank injection application were not adjusted because the average recovery was very high.

Work activities during the study

Adult male workers, who had experience in the work activities, were selected according to the approved protocol and consent form. There were two volunteers for each of the job functions (monitors for sprinkler irrigation, applicators and irrigators for shank injection). Details of work activities are as follows:

a) Sprinkler irrigation: 1) Non-study worker. Injected metam-sodium into water stream by using a closed system; 2) Two study workers. Drove around the field and monitored the sprinkler irrigation equipment for proper application, repaired sprinkler heads as required, and monitored the environmental conditions. These workers were monitored for MITC inhalation exposure for about two hours per replicate.

b) Shank injection: 1) Study workers. Two workers loaded and applied metam-sodium. Each applicator drove the tractor and shank injection equipment, and performed the application. The applicator left the tractor and made repairs as needed, as well as to load metam-sodium. These workers were monitored for MITC inhalation exposure for approximately two hours per replicate. The two application rigs performed application in the field the same time, each applying approximately 5 to 10 acres per hour; 2) Study workers. Two field workers irrigated the field shortly after the application. These workers were monitored for MITC inhalation exposure for two hours per replicate.

Meteorology and measurements

Measurements of meteorology were made including air temperature, soil temperature, wind velocity, wind direction, relative humidity, precipitation and documentation on cloud conditions.

Meteorological data are shown in Table 11. During sprinkler irrigation, the air temperature measured 2 meters above the ground level at 2:30 PM was 91.2 $^{o}$F. During shank injection, the air temperature exceeded 90 $^{o}$F for measurements from 12:30 PM to 4:30 PM. The effects of meteorological conditions to worker exposures could not be quantified. However, lower MITC air concentrations were observed (WSI-2-05 to –06, WSM-1-05 to –06) when the wind speed was high.

Table 11. Meteorological data (one-hour average) during MITC exposure studies using sprinkler irrigation and shank injection in Kern County, California.

| Date | Time | Wind Direction (°) | | Wind Speed (mph) | | Vertical Wind | Air Temp. (°F) | | Soil Temp[b] | RH 1.5M |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1M | 10M | 2M | 10M | Speed[a] | 2M | 10M | (°F) | (%) |
| | | | | | Site 1 - Sprinkler irrigation | | | | | |
| 6/15/99 | 7:30 AM | 312 | 284 | 0.4 | 1.9 | 0.15 | 68.3 | 68.2 | 76.4 | 70 |
| | 8:30 AM | 332 | 309 | 6.7 | 7.8 | 0.42 | 73.7 | 72.8 | 75.8 | 54 |
| | 9:30 AM | 347 | 322 | 6.0 | 6.7 | 0.61 | 76.3 | 75.3 | 76.0 | 50 |
| | 10:30 AM | 338 | 314 | 4.6 | 5.2 | 0.68 | 80.5 | 79.5 | 76.0 | 44 |
| | 11:30 AM | 341 | 325 | 7.0 | 8.1 | 0.80 | 83.3 | 82.2 | 77.0 | 40 |
| | 12:30 PM | 350 | 333 | 7.8 | 8.9 | 0.84 | 86.3 | 85.0 | 78.7 | 36 |
| | 1:30 PM | 6 | 349 | 6.8 | 7.6 | 0.82 | 89.0 | 88.0 | 80.9 | 34 |
| | 2:30 PM | 19 | 2 | 6.3 | 7.0 | 0.81 | 91.2 | 89.8 | 83.5 | 33 |
| | | | | | Site 2 - Shank injection | | | | | |
| 6/27/99 | 6:30 AM | 111 | 99 | 0.2 | 1.1 | 0.04 | 61.3 | 63.1 | 72.0[c] | 73 |
| | 7:30 AM | 113 | 101 | 0.5 | 1.2 | 0.16 | 67.7 | 67.1 | 71.3 | 64 |
| | 8:30 AM | 118 | 105 | 1.1 | 1.5 | 0.33 | 74.4 | 73.5 | 72.1 | 53 |
| | 9:30 AM | 154 | 145 | 1.0 | 0.8 | 0.51 | 81.1 | 80.0 | 74.5 | 41 |
| | 10:30 AM | 279 | 268 | 1.3 | 1.9 | 0.59 | 86.5 | 85.5 | 77.4 | 35 |
| | 11:30 AM | 330 | 317 | 4.1 | 4.9 | 0.72 | 88.3 | 87.7 | 79.8 | 32 |
| | 12:30 PM | 329 | 320 | 6.6 | 7.9 | 0.81 | 90.8 | 90.1 | 82.1 | 30 |
| | 1:30 PM | 339 | 329 | 6.7 | 7.9 | 0.81 | 93.1 | 92.5 | 86.0 | 28 |
| | 2:30 PM | 340 | 327 | 7.3 | 8.5 | 0.78 | 94.7 | 94.3 | 90.3 | 23 |
| | 3:30 PM | 329 | 319 | 5.6 | 6.8 | 0.76 | 96.6 | 96.6 | 93.4 | 20 |
| | 4:30 PM | 322 | 309 | 5.0 | 6.4 | 0.73 | 96.9 | 96.7 | 95.7 | 21 |

(From Table 3, MSTF, 1999a)

[a] Vertical wind speed = 1-hour averages of 15-minute standard deviations of data collected at 10-second intervals. All other meteorological data presented here were collected at 1-minute intervals, then reduced to 1-hour averages.

[b] Soil temperature taken at 3 inches deep.

[c] The area around the probe was wetted with water to simulate preirrigation.

Results

Measured MITC air concentrations near the workers' breathing zone are shown in Table 12. Some workers performed special work tasks such as repairing sprinkler heads in the treated fields, moving sprinkler heads after initiation of applications, attaching the main water line in the treated field, and repairing injection shank rigs. Short-term air concentrations for these workers are grouped based on special work tasks performed and are shown in Table 13. Air concentrations of different replicates of the same work task were combined to reflect the overall exposure estimate for that work task. This Table also shows ADD, SADD, and AADD estimated for adult male workers. One- and 8-hour MITC concentrations were determined based on criteria listed in Table 8 and the results are shown in Table 15 and summarized in Table 16. The report indicated that workers wore respirators while performing certain work tasks, but not while performing other work tasks or traveling. If a respirator was used at a certain time during the sample collection period, reported MITC concentrations could not be adjusted for respiratory protection because MITC concentrations were monitored continuously for about 2 hours.

Air concentrations obtained from the study using shank injection were adjusted to reflect a maximum application rate for metam-sodium (VAPAM® HL) of 75 gallons of formulation (4.26 lbs of metam-sodium/gallon) per acre or 319.5 lbs AI/acre, representing a broadcast application. The exposure estimates are reduced 50% if metam-sodium is applied to planting beds, but not to the area between beds, which is equal approximately to a bed area. In this case, the application rate of metam-sodium (VAPAM® HL) is 37.5 gallons or 159.5 lbs AI per treated acre.

Table 12. MITC found on worker inhalation samples.

| Sample ID[a] | Pump sampling time | | | | Flow | Total | MITC | MITC | MITC |
|---|---|---|---|---|---|---|---|---|---|
| | On (hr:min) | Off (hr:min) | Total (hr:min) | Total (min) | (L/min) | (Liters) | (μg) | (μg/m$^3$)[b] | (ppb)[c] |
| Site 1 - Sprinkler irrigation | | | | | | | | | |
| WSM-1-01 | 7:20 AM | note: sample broken in the field while fixing a sprinkler head | | | | | | | |
| WSM-1-02 | 7:24 AM | 9:35 AM | 2:11 | 131 | 1.0 | 131 | 45.7 | 348.9 | 135.9 |
| WSM-1-03 | 9:34 AM | 11:36 AM | 2:02 | 122 | 1.0 | 122 | 18.1 | 148.4 | 57.8 |
| WSM-1-04 | 9:37 AM | 11:39 AM | 2:02 | 122 | 1.0 | 122 | 19.9 | 163.1 | 63.6 |
| WSM-1-05 | 11:38 AM | 1:39 PM | 2:01 | 121 | 1.0 | 121 | 6.0 | 49.6 | 19.3 |
| WSM-1-06 | 11:40 AM | 1:42 PM | 2:02 | 122 | 1.0 | 122 | 6.7 | 54.9 | 21.4 |
| Site 2 - Shank injection | | | | | | | | | |
| WSI-2-01 | 8:15 AM | 10:35 AM | 2:20 | 140 | 1.0 | 140 | 41.4 | 295.7 | 99.1 |
| WSI-2-02 | 8:17 AM | 10:32 AM | 2:15 | 135 | 1.0 | 135 | 22.0 | 163.0 | 54.6 |
| WSI-2-03 | 10:37 AM | 12:24 PM | 1:47 | 107 | 1.0 | 107 | 18.1 | 169.2 | 56.7 |
| WSI-2-04 | 10:34 AM | 12:28 PM | 1:54 | 114 | 1.0 | 114 | 11.8 | 103.5 | 34.7 |
| WSI-2-05 | 12:27 PM | 2:27 PM | 2:00 | 120 | 1.0 | 120 | 8.8 | 73.3 | 24.6 |
| WSI-2-06 | 12:29 PM | 2:27 PM | 1:58 | 118 | 1.0 | 118 | 10.4 | 88.1 | 29.5 |
| WSA-2-01 | 6:21 AM | 8:17 AM | 1:56 | 116 | 1.0 | 116 | 32.5 | 280.2 | 93.9 |
| WSA-2-02 | 6:28 AM | 8:50 AM | 2:22 | 142 | 1.0 | 142 | 54.2 | 381.7 | 127.9 |
| WSA-2-03 | 8:19 AM | 10:20 AM | 2:01 | 121 | 1.0 | 121 | 147.6 | 1219.8 | 408.8 |
| WSA-2-04 | 8:52 AM | 10:48 AM | 1:56 | 116 | 1.0 | 116 | 81.8 | 705.2 | 236.3 |
| WSA-2-05[d] | 10:22 AM | 12:13 PM | 1:51 | 111 | 1.0 | 111 | 48.0 | 432.4 | 144.9 |
| WSA-2-06[e] | 10:52 AM | 12:13 PM | 1:21 | 81 | 1.0 | 81 | 36.6 | 451.9 | 151.4 |
| CS-2-01 | 6:24 AM | 8:17 AM | 1:53 | 113 | 1.0 | 113 | 32.4 | 286.7 | 96.1 |
| CS-2-02 | 6:26 AM | 8:50 AM | 2:24 | 144 | 1.0 | 144 | 42.7 | 296.5 | 99.4 |
| CS-2-03 | 8:19 AM | 10:20 AM | 2:01 | 121 | 1.0 | 121 | 47.5 | 392.6 | 131.6 |
| CS-2-04 | 8:52 AM | 10:48 AM | 1:56 | 116 | 1.0 | 116 | 54.1 | 466.4 | 156.3 |
| CS-2-05 | 10:22 AM | 12:13 PM | 1:51 | 111 | 1.0 | 111 | 39.8 | 358.6 | 120.2 |
| CS-2-06 | 10:52 AM | 12:13 PM | 1:21 | 81 | 1.0 | 81 | 53.8 | 664.2 | 222.6 |

(From MSTF, 1999a)

[a] Sample ID codes
WSM = Application Monitor - sample on collar
WSI = Irrigator rep. - sample on collar
WSA = Applicator rep. - sample on collar
CS = Cab sample - sample in the cab during application in breathing zone

[b] μg/m$^3$ = μg/1,000 liters of air.

[c] MITC concentrations from the sprinkler irrigation study were adjusted for the average field fortification recovery of 86%; whereas, MITC from the shank injection study were not adjusted because the average recovery was 99%, which was very high. ppb = (μg/m$^3$)/2.984

[d] 2nd tank load lower volume to finish field.

[e] No 2$^{nd}$ tank load loaded or applied.

Table 13. Exposure of adult male workers to MITC during applications of metam-sodium using sprinkler irrigation and shank injection in Kern County, California.[a]

| | Adjusted MITC (ppb)[b] | | | | | ADD[c] (µg/kg/day) | | SADD[d] (µg/kg/day) | | AADD[e] (µg/kg/day) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1-hour | | 8-hour | | | | | | | | |
| Work tasks and observations | Highest | n | Mean | SD | n | Mean | SD | Mean | SD | Mean | SD |
| a). Sprinkler irrigation | | | | | | | | | | | |
| Monitor: Also, repaired and moved sprinkler heads | 136 | 1 | | | | | | | | | |
| Monitor: Monitored the perimeter of treated fields | 63.6 | 4 | 40.5 | 23.4 | 4 | 10.6 | 6.1 | 2.03 | 1.17 | 2.03 | 1.17 |
| All replicates | 136 | 5 | 59.6 | 47.2 | 5 | 15.6 | 12.3 | 2.98 | 2.36 | 2.98 | 2.36 |
| Monitor: Low | 19.3 | | | | | | | | | | |
| Monitor: High | 136 | | | | | | | | | | |
| b). Shank injection | | | | | | | | | | | |
| Irrigator: Also reattached the main water line | 198 | 3 | 140 | 50.2 | 3 | 36.6 | 13.1 | 7.02 | 2.51 | 7.02 | 2.51 |
| Irrigator: High wind speed for the last 2 samples | 69.4 | 3 | 59.2 | 10.1 | 3 | 15.4 | 2.6 | 2.96 | 0.51 | 2.96 | 0.51 |
| Irrigator: Combined all replicates | 198 | 6 | 99.7 | 55 | 6 | 26.0 | 14.4 | 4.99 | 2.75 | 4.99 | 2.75 |
| Irrigator: Low | 49.2 | | | | | | | | | | |
| Irrigator: High | 198 | | | | | | | | | | |
| Loader/applicator: Also repaired injection rigs | 818 | 3 | 515 | 283 | 3 | 135 | 73.9 | 25.8 | 14.2 | 25.8 | 14.2 |
| Loader/applicator: No repair work | 303 | 3 | 260 | 63.0 | 3 | 67.9 | 16.4 | 13.0 | 3.15 | 13.0 | 3.15 |
| Loader/applicator: All replicates | 818 | 6 | 388 | 231 | 6 | 101 | 60.2 | 19.4 | 11.5 | 19.4 | 11.5 |
| Loader/applicator: Low | 188 | | | | | | | | | | |
| Loader/applicator: High | 818 | | | | | | | | | | |
| Inside the tractor cabs: All replicates[f] | 445 | 6 | 275 | 94 | 6 | 71.9 | 24.6 | 13.8 | 4.71 | 13.8 | 4.71 |
| Inside the tractor cabs: Low[f] | 192 | | | | | | | | | | |
| Inside the tractor cabs: High[f] | 445 | | | | | | | | | | |

n is replicate; conc. is concentration. (MSTF, 1999a)

[a] Based on the maximum labeling rate of 75 gallons/acre. For shank injection, the exposure estimates are reduced 50% if metam-sodium is applied to planting beds (not to space between beds) at an application rate of 37.5 gallons/acre.

[b] Determined according to criteria in Table 8. Mean is the arithmetic mean, except values from a single replicate or values indicated as low and high. High and low values are used for 1-hour MITC concentrations because in the long run MITC concentrations would likely fluctuate.

[c] Absorbed daily dosage (ADD) was calculated based on 8 hours/workday. ADD = MITC (µg/$m^3$) x 0.84 $m^3$/h x 8 hours/77 kg body weight.

[d] Seasonal average daily dosage (SADD) was calculated based on 23 workdays in a 120-day season. SADD = ADD x 23 days/120 days

[e] Annual average daily dosage (AADD) was calculated based on 70 workdays in a year. AADD = ADD x 70/365.

[c,d,e] The average dosage of adult females is 0.98 times that of adult males (ratio for females/males = 0.66 $m^3$/h/62 kg ÷ 0.84 $m^3$/h/77 kg = 0.98).

[f] Exposure of applicators who did not exit the cabs.

A.4 Determination of methyl isothiocyanate inhalation exposure to workers during application of metam-sodium through shank injection

On June 13, 2000, Agrisearch Incorporated conducted a field study sponsored by the MSTF to determine MITC inhalation exposure to workers as they applied metam-sodium through shank injection (MSTF, 2001). This study was conducted in part based upon the U.S. EPA OPPTS Harmonized Series 875, "Occupational and Residential Exposure Test Guidelines." The Department of Pesticide Regulation in cooperation with the Committee on Human Research of the University of California, San Francisco, reviewed and approved the study protocol and consent form on May 4, 2000. This study was conducted in accordance with U.S. EPA FIFRA Good Laboratory Practice Standards (40 CFR, Part 160). Metam-sodium was applied according to the recommendations of the TIB dated February 1999, which include mandatory odor mitigation requirement, pre-application irrigation, applying when soil temperature <90 $^{o}$F, soil cap at application, ½ inch water cap immediately post application. Furthermore, metam-sodium was applied when there was no thermal inversion near or at the ground.

This study used an approximately 40 acre bare ground field located in Kern County, California. The test site was subdivided into three replication plots. Sprinkler heads were located along all irrigation pipes spaced 30 feet apart throughout the application plot. The application rate of metam-sodium (VAPAM® HL, 4.26 lbs metam-sodium per gallon) used in the study was 37.5 gallons of formulation (159.75 lbs AI/acre) plus 25 gallons of water per broadcast acre. The applicator drove the tractor (John Deere 8300T Tract Drive) and the shank injection equipment, and performed the application. Metam-sodium was applied only in the bed area and not between beds. Therefore, 75 gallon formulation per treated acre resulted in the application of 37.5 gallon formulation broadcast per acre. The applicator worked in the general area where some formulation had been spilled as well as in the field making adjustments and repairs. Application was made at approximately 5 to 10 acres per hour. As the shank injection unit passed through the field, soil immediately was formed as a planting bed approximately 10 inches deep (as a soil cap). The application was completed in one day. Two experienced workers irrigated the field shortly after application. As mentioned above, each of the three application plots has an area of approximately 13 acres. The first plot was irrigated for about 2 hours. The middle and last plots were each irrigated for about 2.5 hours. This provides a ½ inch water cap to the field post application.

Sample collection

The sorbent tubes, Anasorb CSC (400/200 mg coconut charcoal, SKC Cat. No. 226-09), were used to sample MITC in the breathing zone of workers as they applied metam-sodium by shank injection and during application of a water cap at the shank injection site by sprinkler irrigation. A personal air-sampling pump (Gilian Model HFS 113A) was attached to the belt around the waist of the worker. Tygon® tubing attached to the inlet valve of the pump was placed over the shoulder of the worker and attached to the sorbent tube. A clip was used to attach the charcoal sorbent tube to the collar, thus positioning it in the worker's breathing zone. During shank injection, an additional sampling pump and charcoal tube was operated in the cab of the tractor with the sorbent tube near the breathing zone of the applicator. This sorbent tube measured

application exposure for an applicator who did not leave the cab. The flow rate of the pump was approximately 1 liter/min. The samples were stored in the field for up to 2 days at -56.8 $^{o}$C to -17.3 $^{o}$C. They were frozen on dry ice and shipped via overnight services to the analytical laboratory.

Field fortification recovery

Before the study initiation, the limit of quantitation (LOQ) was determined to be 0.1 µg per sorbent tube or tube section. Agrisearch determined that a silica gel prefilter for moisture was not required because the method try out suggested that the MITC extraction efficiency from charcoal using 20% $CS_2$ in ethyl acetate was greater after high humidity weathering of fortified tubes than after dry weathering of tubes. This means that moisture in the air during the study would not alter MITC extraction efficiency.

A field recovery study of fortified samples was conducted. Sorbent tubes were spiked with MITC solution at 0.5 µg and 10 µg by the analytical laboratory. These samples were shipped on dry ice to the field, where they were stored at –61.9 to –14.7 $^{o}$C for 4 days prior to use in the recovery study. The air sampling system for the recovery study was positioned away from the treated field by several miles and was run at 1.0 Lpm for a 2½-hour collection period, which was approximately the same length of time as the duration of one monitoring period. Results of the field fortification recovery study indicated that MITC was stable in charcoal sorbent tubes weathered on site for 2 ½ hours at a flow rate of 1 Lpm, shipped and stored with test samples, and analyzed with each set of samples. The average field fortification recovery was 89.5% (averaged 90.1% for 0.5 µg and 88.8% for 10 µg spiking). MITC concentrations from this study were adjusted for the average field fortification recovery of 89.5%.

Meteorology and measurements

Measurements of meteorology were made including air temperature, wind speed, wind direction, and vertical wind speed. The general trends of meteorological data during the study were warm (67.3 - 96 $^{o}$F), clear skies; wind speeds were low and relatively consistent.

Results

Measured MITC air concentrations near the workers' breathing zone are shown in Table 14. Some workers performed additional duties such as repairing sprinkler heads in the treated fields. The air concentrations were adjusted to reflect a maximum labeling rate of 75 gallons of formulation per treated acre or 319.5 lbs AI/ treated acre, representing a broadcast application. MITC air concentrations for short-term (1- and 8-hour), intermediate-term, and long-term exposures are shown in Table 15. The short-term MITC concentrations are also summarized in Table 16.

Table 14. Exposure of applicators and irrigators during shank injection application of metam-sodium.[a]

| | Replicate | Monitoring time (h) | MITC air concentration (ppb) | Average[b] | SD[b] |
|---|---|---|---|---|---|
| Irrigators (checked the irrigation system, replaced pipes, etc.) | 5 | 3 | 56.6, 108.8, 63.9, 100.9, 66.5 | 159 | 47.5 |
| Loaders/applicators (loaded and applied metam-sodium) | 3 | 2.5 | 213.1, 225.9, 246.4 | 457 | 33.6 |
| Inside cabs (exposure of an applicator, who did not exit the cab) | 3 | 2.5 | 199.6, 208.5, 190.2 | 399 | 18.3 |

[a] After metam-sodium application, soil immediately was formed as a planting bed approximately 10 inches deep (as a soil cap). The treated field was irrigated for about 2 hours to provide a ½ inch water cap. MITC concentrations, except for the average and standard deviation (SD), reflect an application rate of 37.5 gallons of product (VAPAM® HL) or 159.75 lbs AI per acre.

[b] The average and SD of MITC concentrations were adjusted to reflect an application at 75 gallons of product (VAPAM® HL) or 319.5 lbs AI per acre.

Table 15. Short-, intermediate- and long-term exposures of applicators and irrigators to MITC during shank injection application of metam-sodium.[a]

| | MITC air concentration (ppb) | | | | | | |
|---|---|---|---|---|---|---|---|
| | | 8-hour[b] | | Intermediate-term[c] | | Long-term[d] | |
| | 1-hour[b] | Mean | SD | Mean | SD | Mean | SD |
| Irrigators | 218 | 159 | 47.5 | 10.16 | 3.03 | 10.16 | 3.03 |
| Loaders/applicators | 493 | 457 | 33.6 | 29.20 | 2.15 | 29.20 | 2.15 |
| Inside cabs[e] | 417 | 399 | 18.3 | 25.49 | 1.17 | 25.49 | 1.17 |

[a] After metam-sodium application, soil immediately was formed as a planting bed approximately 10 inches deep (as a soil cap). The treated field was irrigated for about 2 hours to provide a ½ inch water cap. The average and standard deviation (SD) of MITC concentrations were adjusted to reflect a broadcast application at 75 gallons of product (VAPAM® HL) or 319.5 lbs AI/treated acre.

[b] MITC air concentrations were estimated based on criteria shown in Table 8.

[c] Normalized to represent the 24-hour TWA MITC concentration for intermediate-term exposure or (8-hour exposure per day x 8-hour MITC concentration x 23 workdays/(120 days per season x 24 hours per day)).

[d] Normalized to represent the 24-hour TWA MITC concentration for long-term exposure or (8-hour exposure per day x 8-hour MITC concentration x 70 workdays/(365 days per year x 24 hours per day)).

[e] Exposure of an applicator, who did not exit the cab.

Table 16. Summary: Short-term air concentrations of MITC obtained from handler exposure studies.

| Location/ Application methods | Work task | n | Air concentrations of MITC (ppb) 1-hour[a] | 8-hour[b] | Notes |
|---|---|---|---|---|---|
| A.1 Arizona (warm and dry) (ICI Americas Inc., 1992)[c] | | | | | |
| Shank injection | Loader | 10 | 134[d] | 134 (129) | 3-17-min. sampling times |
| | Applicator[e] | 2 | 95 | 76 | 63&78-min. sampling time |
| | Applicator[f] | 4 | 600 | 504 (92) | 60-74-min. sampling times |
| | Applicator[g] | 4 | 1290 | 437 (573) | 60-77-min. sampling times |
| Solid-set sprinklers | Loader | 10 | 914 | 287 (322) | 43-78-min. sampling times |
| | Applicator | 10 | 954 | 500 (374) | 240-254-min. sampling times |
| A.2 Washington (cool and wet) (Zeneca Inc., 1993a)[c] | | | | | |
| Rotary tiller | Loader | 10 | 152[d] | 152 (175) | 3-11-min. sampling times |
| | Applicator[e] | 5 | 832 | 284 (311) | 63-72-min. sampling times |
| | Applicator[f] | 5 | 404 | 224 (141) | 56-63-min. sampling times |
| Center-pivot sprinklers | | | | | |
| | Loader | 5 | 35[d] | 35 (6) | 8-12-min. sampling times |
| | Applicator | 5 | 42 | 29 (8) | 224-241-min. sampling times |
| A.3 Bakersfield, California (warm and dry) (MSTF, 1999a) | | | | | |
| Sprinkler irrigation | Monitor | 1 | 136[h] | | About 4-hour sampling time |
| | Monitors | 4 | 64 | 41 (23)[i] | About 4-hour sampling times |
| Shank injection | Irrigators | 3 | 198 | 140 (50)[j] | About 4-hour sampling times |
| | Irrigators | 3 | 69 | 59 (10)[k] | About 4-hour sampling times |
| | Loaders/applicators | 3 | 818 | 515 (283)[l] | About 4-hour sampling times |
| | Loaders/applicators | 3 | 303 | 260 (63)[m] | About 4-hour sampling times |
| | Inside cabs | 6 | 445 | 275 (94)[n] | About 4-hour sampling times |
| A.4. Kern County, California (warm) (MSTF, 2001) | | | | | |
| Shank injection | Irrigators | 5 | 218 | 159 (48) | 3-3.2-hour sampling times |
| | Loaders/applicators | 3 | 493 | 457 (34) | 1.6-2.5-hour sampling times |
| | Inside cabs | 3 | 417 | 399 (18) | 1.6-2.6-hour sampling times |

[a] 1-hour MITC concentrations represent the highest air concentrations, except those indicated with ([d]).

[b] When applicable, values represent the average (SD).

[c] Exposure data obtained from this study may represent extreme case exposure scenarios because the application procedures, as recommended in the TIB have improved in recent years. The study was included in this document to provide historical perspective.

[d] 1-hour MITC concentrations represent the average air concentrations.

[e] Enclosed cab with a charcoal air filter.

[f] Enclosed cab with a cellulose air filter.

[g] Open cab.

[h] The worker also repaired and moved sprinkler heads.

[i] The workers monitored the perimeter of the treated field.

[j] The irrigators also reattached the main water line.

[k] High wind speed for the last two samples.

[l] The applicators also repaired shank injection rigs.

[m] No repair work.

[n] The cab was not equipped with an air filter.

Note: Two studies (A.1 and A2) shown in the shaded area are retained for historical perspective, only. These studies represent extreme case exposure scenarios and may not be representative of appropriate application methods as are currently required by the Technical Information Bulletin.

Other application methods

Product labels of metam-sodium allow applications other than those methods used in the aforementioned handler exposure studies. Field exposure studies have not been conducted for the following application methods: a) Field application where the entire area is being treated: soil injection (injectors such as blades, fertilizer wheels, plows, etc.), disk applied method, check flood (basin), furrow and border chemigation; b) Field application to beds or rows: drench application on beds or rows; c) Sewer root treatment. Exposure of handlers for these application methods could not be estimated using the available handler exposure studies because 1) The rate of degradation of metam-sodium and hence emission of its degradates, including MITC, could be different depending on application methods, 2) Different cultural practices used in different application methods, 3) Effects of water on degradation of metam-sodium, such as different amount of water is needed for soil injection application versus flood or furrow chemigation, 4) Effects of environmental conditions, such as sun light, wind speed, and temperature on metam-sodium degradation from different application methods.

**B. Exposure of residents to MITC: Adults**

Results of ambient and off-site air monitoring for MITC from six studies (B.2, B.4, B.7, B.8, B.9, and B.10) were used in the estimation of exposure of residents. Exposures for studies B.1, B.3, B.5, and B.6 were included in the following discussion to provide historical perspective, only. Application rates in study B.4 was 318 lbs AI per acre, 159.8 for study B.9, and 319.5 for study B.10. In order to normalize the exposure estimates, metam-sodium application rates were adjusted to reflect a maximum label rate for soil application of 318 lbs AI per acre. The application rates in B.2, B.7, and B.8 were not mentioned in the report because those were ambient MITC monitoring studies; these three studies were not directly associated with specific metam-sodium applications. Therefore, the exposure estimates were not adjusted for the maximum label rate.

B.1 Air monitoring in Contra Costa County (Retained for historical perspective only)

Off-site air monitoring for MITC was conducted after a ground (shank injection) application of metam-sodium at a field in Contra Costa County (Brentwood) during the normal use season in March 1993 (CARB, 1993). Cool air and cool soil temperatures prevailed during this period (air 43.4-73.8 $^{o}$F, soil 53-55 $^{o}$F). The application of metam-sodium (32.7%, 3.18 lbs AI/gal) was done by soil injection at a rate of 18 gal/acre equivalent to 57 lbs AI/acre. The application was set for a depth of 8 inches in soil classified as clay and loam. Following the application, no soil sealing (no ring roller or water seal) was used to reduce MITC emission. The study site covered an area of about 95 acres.

Charcoal-vapor collection tubes (400/200 mg, SKC Cat. No. 226-09) were used to collect air samples. The sampling tube was attached to a support stand. Air was drawn through the sampling tube at an average flow rate of 1.92 L/min using a 12V DC battery-powered vacuum pump. Three samplers were set up at three sites: one approximately 15 yards from the northern perimeter and two approximately 15 yards from the southern perimeter (south west and south east) of the treated field. Duplicate samples were obtained from each of the three sites. The prevailing wind during the study was from the northwest. Samples were collected over a three-

day period. Collection periods ranged from 115 to 950 minutes (15.83 hours). The air volumes ranged from 0.221 $m^3$ to 1.82 $m^3$.

Samples were analyzed by a gas chromatograph equipped with a nitrogen/phosphorous detector. The minimum detection limit was 0.075 μg/sample. The recovery levels for the 1 μg/tube spikes ranged from 68 to 72%, averaging 70%. Results shown in this document are adjusted for the average recovery of 70%. MITC was not detected in three background samples. Short-term air concentrations and estimated average dosages of MITC are shown in Tables 17 (male), 18 (female), and 28 (children). Intermediate- and long-term term air concentrations and estimated average dosages of MITC are shown in Tables 19 (male), 20 (female), and 29 (children). One- and 8-hour MITC concentrations are summarized in Table 31.

B.2 Ambient air monitoring in Kern County during summer 1993

Ambient air monitoring of MITC was conducted in Kern County during the summer of 1993 (CARB, 1994a). Air monitoring was done in July, which represented warm air and warm soil conditions. As indicated in the report, the heaviest use in 1991 occurred from August to December. Application rates of metam-sodium near the sampling stations were not mentioned in the report. Sampling stations were set up at four sites: Shafter, Bakersfield, Lamont and Weed Patch. All samplers were placed on the roofs of single story buildings, except a site in Bakersfield where samplers were placed on the roof of a 3-story building. A sampling tube was elevated about 1.5 meters above the roof by a support stand. Duplicate samples were collected from each of the four sites although not all duplicates were analyzed. Sample tubes were changed approximately every 24 hours. The sampling times ranged from 1345 (22.42 hours) to 1585 minutes (26.42 hours). Eight samples were collected from each sampling site in eight days. The average air flow rate was 1.91 L/min. The average recovery of the field spiked samples was 67%. Results shown in this document are adjusted for the average recovery of 67%. The MDL was 0.03 μg/sample (0.01 $\mu g/m^3$). Short-term air concentrations and estimated average dosages of MITC are shown in Tables 17 (male), 18 (female), and 28 (children). Intermediate- and long-term term air concentrations and estimated average dosages of MITC are shown in Tables 19 (male), 20 (female), and 29 (children). One- and 8-hour MITC concentrations are summarized in Table 31.

B.3 Ambient air monitoring in Kern County during summer 1993 after a shank injection application of metam-sodium to a field (Retained for historical perspective only)

This is essentially an off-site air monitoring study because the study was conducted near a treated field. This field in Kern County was monitored for MITC in the summer of 1993 (CARB, 1994b). This time period represented an "extreme case" application under warm air and warm soil conditions. The weather conditions were in contrast to the study conducted in Contra Costa County (B.1) during March 1993 which represented a "best case" ground application under cool air and cool soil conditions. Metam-sodium was applied by injection at an application rate of 50 gallons per acre equivalent to 155 lbs AI per acre. The application was done over three days in a field about 85 acres. A tractor was used for the application where injection was set at a depth of 10 to 12 inches. Soil type was characterized as sandy loam soil. There was no sealing (no ring roller or water seal) of soil after the application.

Three sampling stations were set 20 yards (southern, western, and northeastern) and one was 40 yards (eastern) from the field perimeter. Sampling equipment and methods were similar to that described in B.1. The average flow rate of air through sampling tubes was 1.88 L/min. Duplicate samples were obtained from each of the four sampling sites, but not all duplicates were analyzed. The sampling times (minutes) ranged from 110 (1.83 hours) to 795 (13.25 hours). Sample series 3 and 4 were exposed to high temperature during storage and the reported values were probably low. One sample (5W) was analyzed later than the other samples and may also be low. A recovery study of field fortification was not conducted. Therefore, the field-spiked recovery of 67% in B.2 (CARB, 1994a) was used to adjust exposure levels. Short-term air concentrations and estimated average dosages of MITC are shown in Tables 17 (male), 18 (female), and 28 (children). Intermediate- and long-term term air concentrations and estimated average dosages of MITC are shown in Tables 19 (male), 20 (female), and 29 (children). One- and 8-hour MITC concentrations are summarized in Table 31.

B.4 Air monitoring for MITC during a fixed-set sprinkler application

Metam-sodium was applied by a fixed-set sprinkler system to a 20-acre fallow field in Kern County, 32-km south of Bakersfield, on August 3, 1993 (Wofford *et al*., 1994). Sprinkler application of metam-sodium was predominant in this area. Fourteen fixed-set sprinkler lines were set east-west across the field, 13.7 meters apart, perpendicular to the main line from a pump located 0.4 km south of the site. Sprinkler heads were spread 9 meters apart on each line for a total sprinkler swath of 400 meters by 200 meters. The field was pre-irrigated for two hours and again for one hour just prior to metam-sodium application. The application lasted for a total of six hours followed by a watering in for 1.5 hours. This represented an "extreme case" exposure scenario because chemigation was done during warm air temperature, low humidity, and warm soil temperature (ranged from 80 to 88 $^{o}$F) at the highest allowable application rate of 100 gallons of metam-sodium (Vapam®) per acre, equivalent to 318 lbs AI per acre.

Air samples of MITC and carbon disulfide ($CS_2$) were collected using two-stage coconut charcoal vapor-collection tubes (400/200 mg, SKC Cat. No. 226-09) mounted to SKC personal air sampling pumps (Model No. 224PCXR7). Silica gel tubes (560/260 mg, SKC Cat. No. 226-10-06) were mounted in front of the charcoal tubes to remove moisture. The flow rate was set at approximately 250 mL/min. Sampling stations were approximately 5 meters (m), 75 m, and 150 m off the perimeter of the treated field. The sample tubes were positioned about 1.2 m above the ground level on metal stakes, except for three sample tubes (4, 7 and 8). The latter were placed at a height of 1.8 m to reduce interference from 1.5-m tall cotton plants. Samples were collected from 10 locations around the field.

Air samples were collected during metam-sodium application (6 hours) and watering-in (1.5 hours) followed by three consecutive 6-hour and four consecutive 12-hour sampling intervals for the total sampling time of 73.5 hours. Air concentration of MITC from a sampling period of 25.5 hours from the first five sampling periods were used to estimate ADD and those of 73.5 hours from nine sampling periods were used to estimate SADD and AADD. Control samples were also collected prior to application. MITC samples were analyzed by gas chromatography equipped with TSD; the MDL was 1.0 µg. The results showed that silica gel media used in sampling interval 2 retained 58-100% of the total MITC passing through the sampling train. However, the silica gel from sampling interval 1 retained 0-4% of the total MITC. MITC

concentrations for both intervals were calculated as the total MITC from the sampling media and silica gel drying tube. Appropriate recovery of field-spiked samples was not available; therefore, a mean recovery of 75% obtained from a trapping efficiency study (5 μg to 1,000 μg) was used to correct field exposure data. Short-term air concentrations and estimated average dosages of MITC are shown in Tables 17 (male), 18 (female), and 28 (children). Intermediate- and long-term term air concentrations and estimated average dosages of MITC are shown in Tables 19 (male), 20 (female), and 29 (children). One- and 8-hour MITC concentrations are summarized in Table 31.

Hydrogen sulfide levels were monitored using Arizona Instrument Corporation Jerome 621 Hydrogen Sulfide Analyzer (minimum detection limit = 3 ppb). This instrument provided instantaneous readings in parts per million. The ranges of hydrogen sulfide concentrations (ppb) after the start of application from 10 sampling sites were "None Detected" (ND = 3 ppb)-76 ppb (1-4 hours), ND (5-7 hours), ND-8 ppb (21-24 hours). $CS_2$ was detected in trace amounts in eight of the 16 samples, but all were under the detection limit of 1.0 μg/segment (4 ppb).

Table 17. Short-term air concentrations and absorbed daily dosages of MITC from ten studies: Exposure of adult males.[a]

| | | Method of application/ sampling site | n[b] | Air conc. (TWA) Mean (ppb) | ADD[c] (µg/kg/day) |
|---|---|---|---|---|---|
| B.1[d] | Contra Costa County (CARB, 1993) (Cool air, 43.4-73.8 °F; Cool soil, 53-55 °F) | Soil injection | 2 | 618 | 514 |
| B.2 | Kern County (CARB, 1994a) | Ambient monitoring | | | |
| | (Warm air & warm soil) | Shafter site | 1 | 1.08 | 0.90 |
| | (Temp. range was not given) | Bakersfield site | 1 | 2.92 | 2.43 |
| | | Lamont site | 1 | 8.32 | 6.92 |
| | | Weed Patch site | 1 | 8.76 | 7.29 |
| B.3[d] | Kern County (CARB, 1994b) (Warm air, 61-92 °F; Warm soil, 79-88 °F) | Soil injection | 3 | 472 | 392 |
| B.4 | Kern County (Wofford *et al*., 1994) | Fixed-set sprinklers | | | |
| | (Warm air, 77-97 °F) | 5 meters | 5 | 1102 | 917 |
| | | 75 meters | 5 | 878 | 731 |
| | | 150 meters | 5 | 468 | 390 |
| B.5[d] | Madera (Zeneca, 1993b) | Fixed-set sprinklers | | | |
| | (Warm soil, 58-88 °F) | 5 meters | 6 | 186 | 155 |
| | (Warm air, 53-94 °F) | 25 meters | 6 | 171 | 142 |
| | | 125 meters | 6 | 118 | 98.5 |
| | | 500 meters | 6 | 22.8 | 19.0 |
| B.6[d] | Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F) | Soil injection | 1 | 236 | 196 |
| B.7 | Bakersfield (Seiber *et al*., 1999) | Ambient monitoring | | | |
| | (Summer) | Lamont: houses | 1 | 5.94 | 4.94 |
| | | Lamont: environment | 1 | 2.53 | 2.10 |
| | | Weedpatch: environ. | 1 | 4.76 | 3.96 |
| | | Shafter: houses | 1 | 6.56 | 5.45 |
| | | Shafter: environment | 1 | 7.71 | 6.40 |
| | (Winter) | Lamont: houses | 1 | 1.21 | 1.01 |
| | | Weedpatch: environ. | 1 | 1.64 | 1.36 |
| | | Arvin: houses | 1 | 0.74 | 0.62 |
| | | Arvin: environ. | 1 | 0.27 | 0.22 |
| B.8 | Lompoc (DPR, 2003b) | Ambient monitoring | 1 | 0.25 | 0.21 |

Table 17 (cont.). Short-term air concentrations and absorbed daily dosages of MITC from ten studies: Exposure of adult males.[a]

| | Method of application/ sampling site | n[b] | Air conc. (TWA) Mean (ppb) | ADD[c] (µg/kg/day) |
|---|---|---|---|---|
| B.9[e] Kern County (MSTF, 1999b) | 150 meters | 1 | 101 | 83.9 |
| (Sprinkler irrigation) | 300 meters | 1 | 52 | 42.8 |
| | 700 meters | 1 | 31 | 25.3 |
| (Shank injection) | 150 meters | 1 | 175 | 145 |
| | 300 meters | 1 | 106 | 87.8 |
| | 486 meters | 1 | 84 | 69.8 |
| B.10 (Krieger *et al*., 1998) | 3-15.2 meters | 5 | 16.3 | [f] |
| (untarped field) | 42.7-50 meters | 2 | 15.0 | [f] |
| (partially tarped field) | 3-15.2 meters | 4 | 7.0 | [f] |
| | 50 meters | 1 | 5.5 | [f] |

[a] 1) Mean (arithmetic) air concentrations and ADDs are based on the short-term and downwind (except B.7 and B.8) air monitoring data, e.g., 24-hour-TWA or closest to 24-hour-TWA, except for B.2 and B.6 where air concentration represents the highest, downwind air concentration.
2) The application rates for B.2, B.7, and B.8 were not known because they were ambient air monitoring studies for MITC, and they were not associated with specific metam-sodium applications. Air concentrations and estimated average dosages of MITC from these three studies were not adjusted for the maximum application rate of metam-sodium.

[b] "n" represents numbers of samples (replicates) collected.

[c] ADD (absorbed daily dosage, µg/kg body weight/day) = [µg/$m^3$ (use short-term air concentration) x inhalation rate ($m^3$/h or $m^3$/day)]/[BW]. Factors used in the calculations for adult males were: body weight = 77 kg, inhalation rate = 0.84 $m^3$/h.

[d] The soil was not "sealed" following application, as is currently required. The MITC air concentrations measured during the application of metam-sodium may not be representative of current practices. The study was included in this document to provide historical perspective.

[e] Represent the highest downwind MITC concentrations.

[f] Not calculated because the absorbed dose is no longer employed in the MITC risk assessment.

Note: Four studies (B.1, B.3, B.5, and B.6) shown in the shaded area are retained for historical perspective, only. The soil in these studies was not "sealed" following application, as is currently required by the Technical Information Bulletin.

Table 18. Short-term air concentrations and absorbed daily dosages of MITC from ten studies: Exposure of adult females.[a]

| | | Method of application/ sampling site | n[b] | Air conc. (TWA) Mean (ppb) | ADD[c] (µg/kg/day) |
|---|---|---|---|---|---|
| B.1[d] | Contra Costa County (CARB, 1993)<br>(Cool air, 43.4-73.8 °F; Cool soil, 53-55 °F) | Soil injection | 2 | 618 | 352 |
| B.2 | Kern County (CARB, 1994a) | Ambient monitoring | | | |
| | (Warm air & warm soil) | Shafter site | 1 | 1.08 | 0.62 |
| | (Temp. range was not given) | Bakersfield site | 1 | 2.92 | 1.66 |
| | | Lamont site | 1 | 8.32 | 4.74 |
| | | Weed Patch site | 1 | 8.76 | 4.99 |
| B.3[d] | Kern County (CARB, 1994b)<br>(Warm air, 61-92 °F; Warm soil, 79-88 °F) | Soil injection | 3 | 472 | 269 |
| B.4 | Kern County (Wofford *et al*., 1994) | Fixed-set sprinklers | | | |
| | (Warm air, 77-97 °F) | 5 meters | 5 | 1102 | 628 |
| | | 75 meters | 5 | 878 | 500 |
| | | 150 meters | 5 | 468 | 267 |
| B.5[d] | Madera (Zeneca, 1993b) | Fixed-set sprinklers | | | |
| | (Warm soil, 58-88 °F) | 5 meters | 6 | 186 | 106 |
| | (Warm air, 53-94 °F) | 25 meters | 6 | 171 | 97.3 |
| | | 125 meters | 6 | 118 | 67.4 |
| | | 500 meters | 6 | 22.8 | 13.1 |
| B.6[d] | Bakersfield (CARB, 1997)<br>(Soil 78-86 °F, air 59.7-98.8 °F) | Soil injection | 1 | 236 | 135 |
| B.7 | Bakersfield (Seiber *et al*., 1999) | Ambient monitoring | | | |
| | (Summer) | Lamont: houses | 1 | 5.94 | 3.38 |
| | | Lamont: environment | 1 | 2.53 | 1.44 |
| | | Weedpatch: environ. | 1 | 4.76 | 2.71 |
| | | Shafter: houses | 1 | 6.56 | 3.73 |
| | | Shafter: environment | 1 | 7.71 | 4.39 |
| | (Winter) | Lamont: houses | 1 | 1.21 | 0.69 |
| | | Weedpatch: environ. | 1 | 1.64 | 0.93 |
| | | Arvin: houses | 1 | 0.74 | 0.42 |
| | | Arvin: environ. | 1 | 0.27 | 0.15 |
| B.8 | Lompoc (DPR, 2003b) | Ambient monitoring | 1 | 0.25 | 0.14 |

Table 18 (cont.). Short-term air concentrations and absorbed daily dosages of MITC from ten studies: Exposure of adult females.[a]

| | Method of application/ sampling site | n[b] | Air conc. (TWA) Mean (ppb) | ADD[c] (µg/kg/day) |
|---|---|---|---|---|
| B.9[e] Kern County (MSTF, 1999b) | 150 meters | 1 | 101 | 57.5 |
| (Sprinkler irrigation) | 300 meters | 1 | 52 | 29.3 |
| | 700 meters | 1 | 31 | 17.3 |
| (Shank injection) | 150 meters | 1 | 175 | 99.2 |
| | 300 meters | 1 | 106 | 60.1 |
| | 486 meters | 1 | 84 | 47.8 |
| B.10 (Krieger *et al*., 1998) | 3-15.2 meters | 5 | 16.3 | [f] |
| (untarped field) | 42.7-50 meters | 2 | 15.0 | [f] |
| (partially tarped field) | 3-15.2 meters | 4 | 7.0 | [f] |
| | 50 meters | 1 | 5.5 | [f] |

[a] 1) Mean (arithmetic) air concentrations and ADDs are based on the short-term and downwind (except B.7 and B.8) air monitoring data, e.g., 24-hour-TWA or closest to 24-hour-TWA, except for B.2 and B.6 where air concentration represents the highest, downwind air concentration.
2) The application rates for B.2, B.7, and B.8 were not known because they were ambient air monitoring studies for MITC, and they were not associated with specific metam-sodium applications. Air concentrations and estimated average dosages of MITC from these three studies were not adjusted for the maximum application rate of metam-sodium.

[b] "n" represents numbers of samples (replicates) collected.

[c] ADD (absorbed daily dosage, µg/kg body weight/day) = [µg/$m^3$ (use short-term air concentration) x inhalation rate ($m^3$/h or $m^3$/day)]/[BW]. Factors used in the calculations for adult females were: body weight = 62 kg, inhalation rate = 0.66 $m^3$/h.

[d] The soil was not "sealed" following application, as is currently required. The MITC air concentrations measured during the application of metam-sodium may not be representative of current practices. The study was included in this document to provide historical perspective.

[e] Represent the highest downwind MITC concentrations.

[f] Not calculated because the absorbed dose is no longer employed in the MITC risk assessment.

Note: Four studies (B.1, B.3, B.5, and B.6) shown in the shaded area are retained for historical perspective, only. The soil in these studies was not "sealed" following application, as is currently required by the Technical Information Bulletin.

Table 19. Intermediate- and long-term air concentrations and average daily dosages of MITC from ten studies: Exposure of adult males.[a]

| | | Method of application/ sampling site | n[b] | Air conc. (TWA) Mean (SD) (ppb) | (μg/kg/day) SADD (SD)[c] | AADD (SD)[d] |
|---|---|---|---|---|---|---|
| B.1[e] | Contra Costa County (CARB, 1993) (Cool air, 43.4-73.8 °F; Cool soil, 53-55 °F) | Soil injection | 7 | 246 | 39.2 | 39.2 |
| B.2 | Kern County (CARB, 1994a) | Ambient monitoring | | | | |
| | (Warm air & warm soil) | Shafter site | 8 | 0.17 | 0.12 | 0.07 |
| | (Temp. range was not given) | Bakersfield site | 8 | 1.01 | 0.73 | 0.43 |
| | | Lamont site | 8 | 2.85 | 2.05 | 1.22 |
| | | Weed Patch site | 8 | 4.09 | 2.95 | 1.75 |
| B.3[e] | Kern County (CARB, 1994b) (Warm air, 61-92 °F; Warm soil, 79-88 °F) | Soil injection | 8 | 229 | 36.6 | 36.6 |
| B.4 | Kern County (Wofford *et al*., 1994) | Fixed-set sprinklers | | | | |
| | (Warm air, 77-97 °F) | 5 meters | 9 | 419 | 66.8 | 66.8 |
| | | 75 meters | 9 | 338 | 54.0 | 54.0 |
| | | 150 meters | 6 | 322 | 51.3 | 51.3 |
| B.5[e] | Madera (Zeneca Inc., 1993b) | Fixed-set sprinklers | | | | |
| | (Warm soil, 58-88 °F) | 5 meters | 13 | 101 | 16.1 | 16.1 |
| | (Warm air, 53-94 °F) | 25 meters | 13 | 95.7 | 15.3 | 15.3 |
| | | 125 meters | 13 | 63.8 | 10.2 | 10.2 |
| | | 500 meters | 13 | 13.1 | 2.08 | 2.08 |
| B.6[e] | Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F) | Soil injection | 6 | 81.9 | 13.1 | 13.1 |
| B.7 | Bakersfield (Seiber *et al*., 1999) | Ambient monitoring | | | | |
| | (Summer) | Lamont: houses | 43 | 1.07 (1.40) | 0.77 (1.01) | 0.46 (0.60) |
| | | Lamont: environ. | 14 | 0.94 (0.86) | 0.68 (0.62) | 0.40 (0.37) |
| | | Weedpatch: environ. | 12 | 1.39 (1.45) | 1.0 (1.04) | 0.60 (0.62) |
| | | Shafter: houses | 45 | 0.46 (1.07) | 0.33 (0.77) | 0.20 (0.46) |
| | | Shafter: environ. | 15 | 0.59 (1.97) | 0.43 (1.42) | 0.25 (0.84) |
| | (Winter) | Lamont: houses | 16 | 0.37 (0.36) | 0.26 (0.26) | 0.16 (0.16) |
| | | Weedpatch: environ. | 8 | 0.50 (0.59) | 0.36 (0.43) | 0.21 (0.26) |
| | | Arvin: houses | 15 | 0.18 (0.21) | 0.13 (0.15) | 0.08 (0.09) |
| | | Arvin: environ. | 6 | 0.13 (0.12) | 0.10 (0.09) | 0.06 (0.05) |
| B.8 | Lompoc (DPR, 2003b) | Ambient monitoring | 1 | 0.0007 | 0.0005 | 0.0003 |

Table 19 (cont.). Intermediate- and long-term air concentrations and average daily dosages of MITC from ten studies: Exposure of adult males.[a]

| | Method of application/ sampling site | Air conc. (TWA) Mean (SD) n[b] | (ppb) | (µg/kg/day) SADD (SD)[c] | AADD (SD)[d] |
|---|---|---|---|---|---|
| B.9[e] Kern County (MSTF, 1999b) | 150 meters | 3 | 55 | 8.68 | 8.68 |
| (Sprinkler irrigation) | 300 meters | 3 | 31 | 5.01 | 5.01 |
| | 700 meters | 3 | 11 | 1.86 | 1.86 |
| (Shank injection) | 150 meters | 3 | 67 | 10.7 | 10.7 |
| | 300 meters | 3 | 39 | 6.18 | 6.18 |
| | 486 meters | 3 | 29 | 4.58 | 4.58 |
| B.10 (Krieger *et al*., 1998) | 3-15.2 meters | 5 | 5.84 | 1.1 ppb[f] | 1.1 ppb[f] |
| (untarped field) | 42.7-50 meters | 2 | 4.90 | 0.9 ppb[f] | 0.9 ppb[f] |
| (partially tarped field) | 3-15.2 meters | 4 | 2.28 | 0.4 ppb[f] | 0.4 ppb[f] |
| | 50 meters | 1 | 1.5 | 0.3 ppb[f] | 0.3 ppb |

[a] 1) Mean (arithmetic) air concentrations, SADDs, and AADDs are based on the intermediate-term and downwind (except B.7 and B.8) air monitoring data. Sample collection times were 69 hours (B.1), 187 hours (B.2 for Shafter site), 66 hours (B.3), and 73.5 hours (B.4).
2) The application rates for B.2, B.7, and B.8 were not known because they were ambient air monitoring studies for MITC, and they were not associated with specific metam-sodium applications. Air concentrations and estimated average dosages of MITC were not adjusted for the maximum application rate of metam-sodium.

[b] "n" represents numbers of samples (replicates) collected.

[c] SADD (seasonal average daily dosage, µg/kg body weight/day) = (ADD x Exposure days in a time period or season) ÷ Days in a time period or season. SADD was calculated based on 23 exposure days in a 120-day season (Haskell, 1994) for exposure to off-site MITC and 78 exposure days in a 90-day period for exposure to ambient MITC (Powell, 1999).

[d] AADD (annual average daily dosage, µg/kg body weight/day) = (ADD x Exposure days in a year) ÷ 365 days/year. AADD was calculated based on 70 exposure days in a year (or 23 x 365/120) (Haskell, 1994) for exposure to off-site MITC and 188 exposure days in a year (365 days) for exposure to ambient MITC (Powell, 1999).

[e] The soil was not "sealed" following application, as is currently required. The MITC air concentrations measured during the application of metam-sodium may not be representative of current practices. The study was included in this document to provide historical perspective.

[f] Normalized (amortized) MITC air concentrations to reflect workdays per season or per year.

Note: Four studies (B.1, B.3, B.5, and B.6) shown in the shaded area are retained for historical perspective, only. The soil in these studies was not "sealed" following application, as is currently required by the Technical Information Bulletin.

Table 20. Intermediate- and long-term air concentrations and average daily dosages of MITC from ten studies: Exposure of adult females.[a]

| | | Method of application/ sampling site | n[b] | Air conc. (TWA) Mean (SD) (ppb) | (µg/kg/day) SADD (SD)[c] | AADD (SD)[d] |
|---|---|---|---|---|---|---|
| B.1[e] | Contra Costa County (CARB, 1993) (Cool air, 43.4-73.8 °F; Cool soil, 53-55 °F) | Soil injection | 7 | 246 | 26.9 | 26.9 |
| B.2 | Kern County (CARB, 1994a) | Ambient monitoring | | | | |
| | (Warm air & warm soil) | Shafter site | 8 | 0.17 | 0.08 | 0.05 |
| | (Temp. range was not given) | Bakersfield site | 8 | 1.01 | 0.50 | 0.30 |
| | | Lamont site | 8 | 2.85 | 1.41 | 0.84 |
| | | Weed Patch site | 8 | 4.09 | 2.02 | 1.20 |
| B.3[e] | Kern County (CARB, 1994b) (Warm air, 61-92 °F; Warm soil, 79-88 °F) | Soil injection | 8 | 229 | 25.0 | 25.0 |
| B.4 | Kern County (Wofford *et al*., 1994) | Fixed-set sprinklers | | | | |
| | (Warm air, 77-97 °F) | 5 meters | 9 | 419 | 45.7 | 45.7 |
| | | 75 meters | 9 | 338 | 36.9 | 36.9 |
| | | 150 meters | 6 | 322 | 35.1 | 35.1 |
| B.5[e] | Madera (Zeneca 1993b) | Fixed-set sprinklers | | | | |
| | (Warm soil, 58-88 °F) | 5 meters | 13 | 101 | 11.0 | 11.0 |
| | (Warm air, 53-94 °F) | 25 meters | 13 | 95.7 | 10.5 | 10.5 |
| | | 125 meters | 13 | 63.8 | 6.96 | 6.96 |
| | | 500 meters | 13 | 13.1 | 1.43 | 1.43 |
| B.6[e] | Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F) | Soil injection | 6 | 81.9 | 8.94 | 8.94 |
| B.7 | Bakersfield (Seiber *et al*., 1999) | Ambient monitoring | | | | |
| | (Summer) | Lamont: houses | 43 | 1.07 (1.40) | 0.53 (0.69) | 0.31 (0.41) |
| | | Lamont: environ. | 14 | 0.94 (0.86) | 0.47 (0.43) | 0.28 (0.25) |
| | | Weedpatch: environ. | 12 | 1.39 (1.45) | 0.69 (0.71) | 0.41 (0.42) |
| | | Shafter: houses | 45 | 0.46 (1.07) | 0.23 (0.53) | 0.13 (0.31) |
| | | Shafter: environ. | 15 | 0.59 (1.97) | 0.29 (0.97) | 0.17 (0.58) |
| | (Winter) | Lamont: houses | 16 | 0.37 (0.36) | 0.18 (0.18) | 0.11 (0.11) |
| | | Weedpatch: environ. | 8 | 0.50 (0.59) | 0.25 (0.29) | 0.15 (0.17) |
| | | Arvin: houses | 15 | 0.18 (0.21) | 0.09 (0.10) | 0.05 (0.06) |
| | | Arvin: environ. | 6 | 0.13 (0.12) | 0.07 (0.06) | 0.04 (0.04) |
| B.8 | Lompoc (DPR, 2003b) | Ambient monitoring | 1 | 0.0007 | 0.0003 | 0.0002 |

Table 20 (cont.). Intermediate- and long-term air concentrations and average daily dosages of MITC from ten studies: Exposure of adult females.[a]

| | | Method of application/ sampling site | Air conc. (TWA) Mean (SD) n[b] | (ppb) | (µg/kg/day) SADD (SD)[c] | AADD (SD)[d] |
|---|---|---|---|---|---|---|
| B.9 | Kern County (MSTF, 1999b) | 150 meters | 3 | 55 | 8.68 | 8.68 |
| | (Sprinkler irrigation) | 300 meters | 3 | 31 | 5.01 | 5.01 |
| | | 700 meters | 3 | 11 | 1.86 | 1.86 |
| | (Shank injection) | 150 meters | 3 | 67 | 10.7 | 10.7 |
| | | 300 meters | 3 | 39 | 6.18 | 6.18 |
| | | 486 meters | 3 | 29 | 4.58 | 4.58 |
| B.10 | (Krieger *et al*., 1998) | 3-15.2 meters | 5 | 5.84 | 1.1 ppb[f] | 1.1 ppb[f] |
| | (untarped field) | 42.7-50 meters | 2 | 4.90 | 0.9 ppb[f] | 0.9 ppb[f] |
| | (partially tarped field) | 3-15.2 meters | 4 | 2.28 | 0.4 ppb[f] | 0.4 ppb[f] |
| | | 50 meters | 1 | 1.5 | 0.3 ppb[f] | 0.3 ppb |

[a] 1) Mean (arithmetic) air concentrations, SADDs, and AADDS are based on the intermediate-term and downwind (except B.7 and B.8) air monitoring data, e.g., sample collection times were 69 hours (B.1), 187 hours (B.2 for Shafter site), 66 hours (B.3), and 73.5 hours (B.4). 2) The application rates for B.2, B.7, and B.8 were not known because they were ambient air monitoring studies for MITC, and they were not associated with any metam-sodium applications. Air concentrations and estimated average dosages of MITC were not adjusted for the maximum application rate of metam-sodium.

[b] "n" represents numbers of samples (replicates) collected.

[c] SADD (seasonal average daily dosage, µg/kg body weight/day) = (ADD x Exposure days in a time period or season) ÷ Days in a time period or season. SADD was calculated based on 23 exposure days in a 120-day season (Haskell, 1994) for exposure to off-site MITC and 78 exposure days in a 90-day period for exposure to ambient MITC (Powell, 1999).

[d] AADD (annual average daily dosage, µg/kg body weight/day) = (ADD x Exposure days in a year) ÷ 365 days/year. AADD was calculated based on 70 exposure days in a year (or 23 x 365/120) (Haskell, 1994) for exposure to off-site MITC and 188 exposure days in a year (365 days) for exposure to ambient MITC (Powell, 1999).

[e] The soil was not "sealed" following application, as is currently required. The MITC air concentrations measured during the application of metam-sodium may not be representative of current practices. The study was included in this document to provide historical perspective.

[f] Shown as normalized (amortized) MITC air concentrations to reflect workdays per season or per year.

Note: Four studies (B.1, B.3, B.5, and B.6) shown in the shaded area are retained for historical perspective, only. The soil in these studies was not "sealed" following application, as is currently required by the Technical Information Bulletin.

B.5 Exposure estimates for residents to MITC (Retained for historical perspective only)

This study was conducted to monitor off-site movement of MITC during and after an application of metam-sodium (Zeneca Inc., 1993b). Metam-sodium (Busan 1020 and Soil-Prep, 32.7%) was

applied to a field of 6.69 acres in Madera County, near Firebaugh, California, on May 2 through May 4, 1992 using fixed-set sprinklers. The test site was cultivated and disced. The soil was classified as Calhi Loamy Sand with moderate alkalinity. The application rate was the maximum label rate of 100 gallons per acre equivalent to 318 lbs AI per acre. The soil temperatures during the study (three inches into the soil) ranged from 58 to 88 $^{o}$F and the air temperatures ranged from 53 to 94 $^{o}$F.

Ambient air concentrations of MITC were monitored at 5, 25, 125, and 500 meters from the downwind edge of the application zone during application and for 48 hours after application. Charcoal vapor-collection tubes (400/200 mg, SKC Cat. No. 226-09) were used to collect samples. The sample tubes were attached to air sampling pumps (SKC Cat. No. 228-501) by flexible tubing. The charcoal tube was preceded by a silica gel drying tube (200/100 mg, SKC Cat. No. 226-10-06) and a plastic cassette containing a glass fiber filter and support pad; these were used to trap moisture and dust particles, respectively. The charcoal and silica gel tubes were placed inside a hollow plastic tube to protect them from physical damage and hung from the T-post at a height of 1.5 meters above the ground level. The pump was set to operate at a flow rate of 1.0 liter per minute. Charcoal tubes were changed every four hours.

Field fortification recovery studies were conducted on May 2 and May 3. Duplicate sets of charcoal sample tubes were spiked at three rates: 0.986 μg, 98.6 μg, and 986 μg. Preparation and setting of these tubes were similar to that of MITC sample collection tubes. These tubes were placed two to three miles upwind from the application site. Samples were exposed to the environment for four hours. The field fortification recoveries ranged from 92.3 to 122 percent. Average percent recoveries were 97.8 and 100 percent for the studies in two days. Results shown in this document were not adjusted for the field fortification recoveries because the average recoveries were very high.

For residents' exposure estimation, average concentration of MITC at each distance collected for 24 hours was used. Short-term air concentrations and estimated average dosages of MITC are shown in Tables 17 (male), 18 (female), and 28 (children). Intermediate- and long-term term air concentrations and estimated average dosages of MITC are shown in Tables 19 (male), 20 (female), and 29 (children). One- and 8-hour MITC concentrations are summarized in Table 31.

B.6 Air monitoring in Kern County in August 1995 (Retained for historical perspective only)

Ambient air monitoring for MITC was performed after a ground injection application of metam-sodium in Kern County in August 1995 (CARB, 1997). The temperature in soil ranged from 78 to 86 $^{o}$F and that for ambient air ranged from 59.7 to 98.8 $^{o}$F. The wind speed ranged from 1.4 to 8.0 miles per hour. The application of metam-sodium (33%, 3.1 lbs AI/gal) was done by soil injection at a rate of 50 gal/acre equivalent to 155 lbs AI/acre. The application was set for a depth of 10 to 12 inches in soil. A liquid fertilizer and Till-it zinc were also applied. The study site covered an area of about 80 acres.

Charcoal vapor-collection tubes (400/200 mg, SKC Cat. No. 226-09) were used to collect air samples. The sampling tube was attached to a support stand. Air was drawn through the sampling tube at an average flow rate of 1.9 L/min using a battery-powered double-headed

vacuum pump. The tubes were approximately 1.5 meters above the ground. Five samplers were set up: one approximately 12 yards from the eastern perimeter, two about 13 yards from the southern perimeter, one about 13 yards from the northern perimeter, and one about 20 yards from the western side of the treated field. The prevailing wind during the study was from the northeast and southeast. Samples were collected over a four-day period. Collection periods ranged from 345 minutes to 815 minutes (13.6 hours). The air volumes ranged from 0.66 to 1.5 $m^3$.

Samples were analyzed by a gas chromatograph equipped with a nitrogen/phosphorous detector. The recovery of field spike samples averaged 73%. Results shown in this document were adjusted for the field fortification recovery of 73%. MITC was detected in the background samples. However, the MITC results were not adjusted for the low background levels, which ranged from 0.08 to 0.18 ppb. Short-term air concentrations and estimated average dosages of MITC are shown in Tables 17 (male), 18 (female), and 28 (children). Intermediate- and long-term term air concentrations and estimated average dosages of MITC are shown in Tables 19 (male), 20 (female), and 29 (children). One- and 8-hour MITC concentrations are summarized in Table 31.

The XAD-7 sampling tubes (SKC Cat. No. 226-97) were used to collect air samples for analysis of methyl isocyanate (MIC). The sampling tubes are 8 mm x 110 mm with 175 mg XAD-7 in each of the primary and secondary tubes. Sampling locations and sample collection periods are essentially the same as those for MITC. The flow rate for the XAD-7 tube was set at 70 mL/min. But, the actual flow rate was measured at 90 mL/min. Subsequent to sampling, all tubes were stored on dry ice in the field and on blue ice for delivery. In the laboratory, they were stored in a freezer until analysis was complete.

Samples were desorbed with acetonitrile and analyzed by a high-performance liquid chromatograph equipped with a fluorescence detector. The limit of detection in terms of air concentrations was 74 $ng/m^3$ or 0.032 parts per billion by volume (ppbv, as it is used by the California Air Resources Board). The limit of quantitation in terms of air concentration was 0.58 $\mu g/m^3$ or 0.25 ppbv. Results showed downwind air concentrations of MIC ranged from 1.0 to 5.8 $\mu g/m^3$ or 0.4 to 2.5 ppbv. Overall MIC air concentrations ranged from 0.6 to 5.8 $\mu g/m^3$ or 0.3 to 2.5 ppbv.

B.7 Air monitoring in Bakersfield-area townships in Summer, 1997, and Winter, 1998

Seiber *et al*. (1999) conducted a study to monitor ambient air concentrations of MITC in Bakersfield-area townships during summer, 1997, and winter, 1998. These townships were Lamont, Weedpatch, and Shafter for summer monitoring and Lamont, Weedpatch, and Arvin for winter monitoring. MITC was monitored indoors and/or outdoors (AM and/or PM samples) for each sampling station.

The sampling equipment consisted of coconut charcoal-filled glass tubes connected to a battery- or an AC-powered pump. Sampling occurred at flow rates of 1.0-1.5 L/min for periods of approximately 11-12 hours. During summer, sampling took place in May, June, July, and August of 1997. During winter, sampling took place in January and March of 1998. Each sampling station had two colocated samples. Samples were stored at –20 $^oC$ for 2-3 months

before analysis. The analysis was accomplished by using nitrogen-phosphorus thermionic gas chromatography.

There were known applications of metam-sodium in those townships where the air monitoring study took place. However, data collected from those sampling stations did not represent absolute downwind air concentrations of MITC. Overall for the summer samples, the wind direction from the treated fields toward the sampling stations occurred 0-44% of the time during the various sampling periods. For the winter samples, the range was 2-16%. The submitted report indicated that during an application season, concentrations of volatile components related to the pesticide application will typically be elevated in air basin, and remain so until the application season has ended. The report concluded that this phenomenon would also lead to elevated residues in townships contained within the air basin without the necessity of a wind vector for carrying residues from a specific application site.

The percentage of recovery was determined from duplicate spikes of 740 ng MITC on to air sampling tubes (2 g of coconut charcoal). The airflow rates passing the tubes were maintained at 1.5-1.6 L/min for 11-12 hours using battery-powered pumps. The MITC recovery for spiked air and from directly spiked charcoal was about 80%, indicating good trapping efficiency of charcoal air sampling tubes for MITC in air. The winter spikes had an average recovery of 80.3% (79.4 and 81.2%) for low (≈2 µg) and high (≈20 µg) spikes. However, percent recoveries for summer spikes were 82.0 (May), 61.8 (June), 71.0 (July), and 53.2 (August). Air concentrations of MITC obtained from the study were adjusted by using these field-spiked recoveries. The LOQ of MITC in field air is on the order of 60-70 ng/m$^3$ (0.020-0.023 ppb). When it is necessary, half of the LOQ (32.5 ng/m$^3$ or 0.01 ppb) was used for samples indicated less than LOQ (<LOQ).

Seiber *et al*. (1999) also conducted a study to determine freezer storage stability of MITC. Results from the freezer spikes, which were kept in the freezer for 2-3 months, showed an overall recovery of 79.4 ± 10.8%. This percentage of recovery indicated that MITC was stable on coconut charcoal at freezer temperature for about 2-3 months. Since MITC data were adjusted for field-spiked recoveries, the recovery from the storage stability was not used to adjust the MITC data.

ADD, SADD, and AADD were calculated from daily air concentration of MITC, which included morning (AM) and afternoon (PM) samples. These samples were collected from indoor and/or outdoor sampling stations. Combined MITC air concentration data from AM and PM samples are more representative than using AM or PM samples alone. It was assumed that residents would be exposed to MITC available in the AM and PM periods, and indoor and/or outdoor sites. ADD was estimated from the highest daily MITC air concentration of each sampling station; SADD and AADD were estimated from the average of daily MITC concentrations of each sampling station during summer or winter. Short-term air concentrations and estimated average dosages of MITC are shown in Tables 17 (male), 18 (female), and 28 (children). Intermediate- and long-term term air concentrations and estimated average dosages of MITC are shown in Tables 19 (male), 20 (female), and 29 (children). One- and 8-hour MITC concentrations are summarized in Table 31.

B.8 Air monitoring study in Lompoc

Ambient air concentrations of MITC and other pesticides in Lompoc (DPR, 2003b) were measured to establish screening levels for the Lompoc Pesticide Air Monitoring Project (Phase I). The screening levels represent air concentrations that are health protective for all individuals, including sensitive sub-populations (e.g., six-year-old children).

The report did not mention the sampling method, number of replicates, specific location of the sampling site, analytical methods, or recovery study. However, the maximum ambient 24-h TWA MITC measured in Lompoc was 0.753 $\mu g/m^3$. The seasonal average air concentrations in Lompoc were averages of daily air levels at the sampling location with highest air concentration. For calculation of exposure, values for nondetects assumed 1/2 LOD and trace assumed 1/2 (LOD + LOQ). The seasonal average of air concentrations was 0.002 $\mu g/m^3$. Short-term air concentrations and estimated average dosages of MITC are shown in Tables 17 (male), 18 (female), and 28 (children). Intermediate- and long-term term air concentrations and estimated average dosages of MITC are shown in Tables 19 (male), 20 (female), and 29 (children). One- and 8-hour MITC concentrations are summarized in Table 31.

B.9 Off-site air movement of MITC from the application of metam-sodium through shank injection and sprinkler irrigation in Kern County

In June 1999, Agrisearch Incorporated conducted a study sponsored by the MSTF to determine MITC off-site air movement from the application of metam-sodium through shank injection and sprinkler irrigation (MSTF, 1999b). Two plots of fields located in Bakersfield, California were used in the study. The shank injection method was used to apply metam-sodium at a rate of 75 gallons of metam-sodium formulation (VAPAM® HL, 42% AI, 4.26 lbs of metam-sodium per gallon) per treated acre (319.5 lbs AI/acre) to a 79-acre carrot field. The application rate was approximately 37.5 gallons per acre if areas between beds were taken into account. During the application of metam-sodium as the shank injection unit passed through the field, soil was formed as a planting bed approximately 10 inches deep (as a final soil cap). The shank injection application employed two injection rigs and the application was completed in one day. The sprinkler irrigation method was employed to apply metam-sodium at a rate of 75 gallon formulation per acre to an 80-acre carrot field. The sprinkler application was conducted over a four-day period, based on 20 acres/day coverage. Both application methods followed recommendations according to the TIB dated February 1999.

Odor control

The odor control measures for sprinkler irrigation as required by the product label and the TIB included:

- pre-application irrigation.
- applied when air temperature <90 $^oF$ and wind speed was ≤7 mph.
- applied when there was no thermal inversion near or at the ground.
- applied a ½ inch water cap immediately post application.
- applied an additional ½ inch water cap within 24 hours postapplication.

The odor control measures for shank injection as required by the product label and the TIB included:

- pre-application irrigation.
- applied when soil temperature <90 $^{o}$F.
- created soil cap at application.
- applied a ½ inch water cap immediately postapplication.

Charcoal vapor-collection tubes (400/200 mg, SKC Cat. No. 226-09) were used to collect MITC in air. The tubes were connected to a personal air sampling pump (Gilian Model HFS 113A) using Tygon® tubing. The unit was attached to a metal stand and the air inlet of the tube was 1.5 meter above the ground. The flow rate of the pump was approximately 1 L/min. Each tube was used to collect an air sample for four hours.

Before the study initiation, the LOQ was determined to be 0.1 μg per sorbent tube or tube section. Also, Agrisearch determined that a prefilter for moisture (silica gel) was not required because the method try out data suggested that the MITC extraction efficiency from charcoal using 20% $CS_2$ in ethyl acetate was greater after humidity weathering of fortified tubes than after dry weathering of tubes.

A field recovery study of fortified samples was conducted. Sorbent tubes were spiked with aliquots of the fortification solution, which was supplied by the analytical laboratory, at 0.5 μg and 10 μg. Three replicate samples at the two rates were fortified at each site on each date. The air sampling system was located upwind of the treated field and was run at 1.0 liter per minute for a 4-hour collection period. However, upwind air samples for two of the sites appeared to be contaminated with MITC. Results of the studies revealed that the highest MITC air concentrations were not observed at the same sampling site. This led to the conclusion that the wind directions changed during the study periods. In other words, not all sampling stations were located in the downwind direction. Results of field fortification recoveries ranged from 44 to 3,486% for a sprinkler irrigation study. However, the average recovery was 86 ± 7% (range 74-99%) after the background MITC, which was found in control samples, was subtracted from fortified samples that showed very high recoveries. The average field fortification recovery during a study of shank injection method was 99 ± 13% (range 81-117%). MITC concentrations obtained from the sprinkler irrigation study were adjusted to reflect the average field fortification recovery of 86%, but MITC concentrations obtained from the study using shank application of metam-sodium were not adjusted because the average recovery was very high.

Tables 21 and 22 show short- and intermediate-term MITC air concentrations at various distances from the treated fields after the applications of metam-sodium using sprinkler irrigation and shank injection methods. Air concentrations obtained from the study using shank injection were adjusted to reflect a label rate of 75 gallons of metam-sodium formulation (VAPAM® HL) per treated acre (319.5 lbs AI/acre). For short-term exposure (for calculation of ADD), a daily MITC air concentration represents the TWA air concentration of 6 samples collected approximately for four hours per sample. For intermediate-term exposure (for calculation of SADD), an air concentration represents an average of TWA air concentrations from days 1-4 of each distance of a sampling station. These intermediate-term air concentrations from all stations for the same distance were averaged and used in the calculation of AADD.

Exposure of residents was calculated for adult males and females, and children. Off-site MITC concentrations from this study are not the same as a typical ambient air monitoring study where sampling stations were not set near treated fields. Twenty-three exposure days in a 120-day period were used to calculate intermediate-term exposure and 70 days in 365 days for long-term exposure. Results are shown in Tables 23 (male), 24 (female), 28 and 29 (children). These results are also shown in Tables 17, 18, 19, 20, and 31.

Table 21. Off-site MITC air concentrations after the application of metam-sodium using sprinkler irrigation.[a]

| Distance (m) | Sampling station | Short-term (TWA, ppb)[b] (for ADD) Day 1 | Day 2 | Day 3 | Day 4 | Intermediate-term (ppb) (for SADD and AADD) Days 1-4[c] | All stations[d] |
|---|---|---|---|---|---|---|---|
| 150 | A | 101 | 77 | 40 | 35 | 63 | |
| | B | 33 | 57 | 82 | 32 | 51 | 55 |
| | D | 31 | 56 | 82 | 30 | 50 | |
| 300 | A | 44 | 49 | 23 | 22 | 35 | |
| | B | 23 | 37 | 46 | 22 | 32 | 31 |
| | C | 8 | 33 | 52 | 18 | 27 | |
| 700 | A | 14 | 31 | 4.5 | 8.5 | 14 | |
| | B | 6.6 | 19 | 17 | 6.8 | 12 | 11 |
| | C | 3.6 | 11 | 10 | 8.4 | 8.3 | |
| 970 (upwind) | A | 0.08 | 2.9 | 2.0 | 2.9 | 2.0 | |
| | B | 0.21 | 12.7 | 1.2 | 2.5 | 4.1 | |

[a] MSTF, 1999b.

[b] Daily MITC air concentrations collected at each sampling station for Days 1-4.

[c] An average of daily MITC air concentrations for each sampling station.

[d] Average MITC concentrations from intermediate-term MITC of all stations for the same distance.

Table 22. Off-site MITC air concentrations after the application of metam-sodium using shank injection.[a]

| Distance (m) | Sampling station | Short-term (ppb)[b] (for ADD) Day 1 | Day 2 | Day 3 | Day 4 | Intermediate-term (ppb) (for SADD and AADD) Days 1-4[c] | All stations[d] |
|---|---|---|---|---|---|---|---|
| 150 | A | 140 | 175 | 55 | 6.5 | 94 | |
| | B | 71 | 98 | 28 | 5.3 | 51 | 67 |
| | D | 80 | 110 | 34 | 5.4 | 57 | |
| 300 | A | 68 | 106 | 42 | 7.3 | 56 | |
| | B | 39 | 53 | 28 | 6.4 | 32 | 39 |
| | C | 41 | 45 | 23 | 5.4 | 29 | |
| 486 | A | 36 | 84 | 26 | 9.0 | 39 | |
| | B | 32 | 47 | 24 | 6.7 | 28 | 29 |
| | C | 24 | 32 | 17 | 6.0 | 20 | |
| 837 (upwind) | A | 78 | 18 | 28 | 4.7 | 33 | |
| | B | 106 | 62 | 28 | 4.0 | 51 | |

[a] MSTF, 1999b.

[b] TWA of MITC air concentrations collected at each sampling station for Days 1-4.

[c] An average of daily MITC air concentrations for each sampling station.

[d] Average MITC concentrations from intermediate-term MITC of all stations for the same distance.

Table 23. Exposure of male residents to off-site MITC generated from the application of metam-sodium.

1. Sprinkler irrigation[a]

| Distance (m) | Sampling station | | Short-term exposure MITC (TWA) (ppb) | Short-term exposure ADD[b] (µg/kg/day) | Sampling station | Intermediate- and long-term exposure MITC (TWA, ppb) (Days 1-4) | | Intermediate- and long-term exposure (µg/kg/day) SADD[c] | AADD[d] |
|---|---|---|---|---|---|---|---|---|---|
| 150 | D | Low | 30 | 24.7 | D | Low | 50 | 7.94 | 7.94 |
| | A | High | 101 | 83.9 | A | High | 63 | 10.0 | 10.0 |
| | | | | | | Mean | 55 | 8.68 | 8.68 |
| 300 | C | Low | 8 | 6.39 | C | Low | 27 | 4.37 | 4.37 |
| | C | High | 52 | 42.8 | A | High | 35 | 5.49 | 5.49 |
| | | | | | | Mean | 31 | 5.01 | 5.01 |
| 700 | C | Low | 3.6 | 3.06 | C | Low | 8.3 | 1.33 | 1.33 |
| | A | High | 31 | 25.3 | A | High | 14 | 2.29 | 2.29 |
| | | | | | | Mean | 11 | 1.86 | 1.86 |
| 970 | A | Low | 0.08 | 0.06 | A | Low | 2 | 0.31 | 0.31 |
| (upwind) | B | High | 12.7 | 10.5 | B | High | 4.1 | 0.66 | 0.66 |

2. Shank injection[a]

| Distance (m) | Sampling station | | Short-term exposure MITC (TWA) (ppb) | Short-term exposure ADD[b] (µg/kg/day) | Sampling station | Intermediate- and long-term exposure MITC (TWA, ppb) Days 1-4 | | Intermediate- and long-term exposure (µg/kg/day) SADD[c] | AADD[d] |
|---|---|---|---|---|---|---|---|---|---|
| 150 | D | Low | 5.4 | 4.45 | B | Low | 51 | 8.04 | 8.04 |
| | A | High | 175 | 145 | A | High | 94 | 15.0 | 15.0 |
| | | | | | | Mean | 67 | 10.7 | 10.7 |
| 300 | C | Low | 5.4 | 4.45 | C | Low | 29 | 4.58 | 4.58 |
| | A | High | 106 | 87.8 | A | High | 56 | 8.90 | 8.90 |
| | | | | | | Mean | 39 | 6.18 | 6.18 |
| 486 | C | Low | 6 | 5.0 | C | Low | 20 | 3.20 | 3.20 |
| | A | High | 84 | 69.8 | A | High | 39 | 6.18 | 6.18 |
| | | | | | | Mean | 29 | 4.58 | 4.58 |
| 837 | B | Low | 4 | 3.34 | A | Low | 33 | 5.17 | 5.17 |
| (upwind) | B | High | 106 | 88.4 | B | High | 51 | 8.04 | 8.04 |

[a] MSTF, 1999b.

[b] ADD (absorbed daily dosage) = [µg/day (short-term MITC) x inhalation rate ($m^3$/day)]/[BW]. Factors used in the calculations were: body weight = 77 kg, inhalation rate = 21.4 $m^3$/day.

[c] SADD (seasonal average daily dosage) = (ADD x Exposure days in a season) ÷ Days in a season. SADD was calculated using 23 exposure days in a 120-day season (Haskell, 1994).

[d] AADD (annual average daily dosage) = (ADD x Exposure days/year) ÷ 365 days. AADD was calculated using 70 exposure days/year year (Haskell, 1994) for exposure to off-site MITC.

Table 24. Exposure of female residents to off-site MITC generated from the application of metam-sodium.

1. Sprinkler irrigation[a]

| Distance (m) | Short-term exposure: Sampling station | | MITC (TWA) (ppb) | ADD[b] (µg/kg/day) | Intermediate- or long-term exposure: Sampling station | | MITC (TWA, ppb) Days 1-4 | (µg/kg/day) SADD[c] | AADD[d] |
|---|---|---|---|---|---|---|---|---|---|
| 150 | D | Low | 30 | 16.94 | D | Low | 50 | 5.44 | 5.44 |
| | A | High | 101 | 57.5 | A | High | 63 | 6.86 | 6.86 |
| | | | | | | Mean | 55 | 5.95 | 5.95 |
| 300 | C | Low | 8 | 4.38 | C | Low | 27 | 2.99 | 2.99 |
| | C | High | 52 | 29.3 | A | High | 35 | 3.76 | 3.76 |
| | | | | | | Mean | 31 | 3.43 | 3.43 |
| 700 | C | Low | 3.6 | 2.09 | C | Low | 8.3 | 0.91 | 0.91 |
| | A | High | 31 | 17.3 | A | High | 14 | 1.57 | 1.57 |
| | | | | | | Mean | 11 | 1.28 | 1.28 |
| 970 (upwind) | A | Low | 0.08 | 0.04 | A | Low | 2 | 0.22 | 0.22 |
| | B | High | 12.7 | 7.21 | B | High | 4.1 | 0.45 | 0.45 |

2. Shank injection[b]

| Distance (m) | Short-term exposure: Sampling station | | MITC (TWA) (ppb) | ADD[b] (µg/kg/day) | Intermediate- and long-term exposure: Sampling station | | MITC (TWA, ppb) Days 1-4 | (µg/kg/day) SADD[c] | AADD[d] |
|---|---|---|---|---|---|---|---|---|---|
| 150 | D | Low | 5.40 | 3.05 | B | Low | 51 | 5.51 | 5.51 |
| | A | High | 175 | 99.2 | A | High | 94 | 10.3 | 10.3 |
| | | | | | | Mean | 67 | 7.33 | 7.33 |
| 300 | C | Low | 5.40 | 3.05 | C | Low | 29 | 3.14 | 3.14 |
| | A | High | 106 | 60.1 | A | High | 56 | 6.09 | 6.09 |
| | | | | | | Mean | 39 | 4.23 | 4.23 |
| 486 | C | Low | 6 | 3.43 | C | Low | 20 | 2.19 | 2.19 |
| | A | High | 84 | 47.8 | A | High | 39 | 4.23 | 4.23 |
| . | | | | | | Mean | 29 | 3.14 | 3.14 |
| 837 (upwind) | B | Low | 4 | 2.28 | A | Low | 33 | 3.54 | 3.54 |
| | B | High | 106 | 60.5 | B | High | 51 | 5.51 | 5.51 |

[a] MSTF, 1999b.

[b] ADD (absorbed daily dosage) = [µg/day (short-term MITC) x inhalation rate ($m^3$/day)]/[BW]. Factors used in the calculations were: body weight = 62 kg, inhalation rate = 11.8 $m^3$/day.

[c] SADD (seasonal average daily dosage) = (ADD x Exposure days in a season) ÷ Days in a season. SADD was calculated using 23 exposure days in a 120-day season (Haskell, 1994).

[d] AADD (annual average daily dosage) = (ADD x Exposure days/year) ÷ 365 days. AADD was calculated using 70 exposure days/year year (Haskell, 1994) for exposure to off-site MITC.

B.10. Off-site air monitoring from drip irrigation of metam-sodium in untarped and partially tarped fields

Metam-sodium product labels allow an application of metam-sodium through a drip irrigation system. This method of application is not as widely used in agricultural production as other application methods, such as soil injection, sprinkler irrigation, or rotary tiller or power mulcher. This is because there are some limitations on the use of a drip irrigation system according to the product labels. The limitations include a) the ground must be in seed-bed condition, no clods larger than ½" in diameter, b) beds must be shaped and ready for planting, and c) soil moisture must be 50% of field capacity in the top 2-3" at time of application. Furthermore, application must be continuously supervised because an adequate concentration of metam-sodium must be present at the time of weed seed germination in order to be effective.

Residents (adults and children) may be exposed to off-site MITC generated during and after the application of metam-sodium by drip irrigation. This system was generally thought to generate low levels of MITC in air and it could be used to mitigate MITC exposure. In 1997, Krieger *et al*. (1998) conducted a study to measure off-site downwind MITC concentrations from the application of metam-sodium using the drip irrigation system to untarped and partially tarped fields. Metam-sodium (Vapam® HL, 42-43%, 4.26 lbs AI/gallon) was applied to Field 1 (untarped, 9.9 acres) and Field 2 (partially tarped with 1.5 mm plastic mulch, 3.0 acres) at the maximum label rate of 700 L/ha (318.5 lbs AI/acre) by drip irrigation. Metam-sodium was applied at a depth of about 10 cm for both fields, which were located in Orange County, California. Treatment of Field 1 began at about 1800 hours on February 14, 1997, and was completed 4 hours later. Treatment of Field 2 began at about 1820 hours on March 28, 1997, and was completed 2.4 hours later. The report did not provide information on the "partially tarped field" as to what percentage of the field was covered with tarpaulin. This study was not conducted in accordance with the U.S. EPA Good Laboratory Practice standards (40 CFR, Part 160).

Air Monitoring study

The air sampling masts were set up around the fields and along 2 directions downwind of the fields, giving a total of 10 masts per field. For the untarped field, these masts were located 10, 14, 20, 25, 50, 140, and 164 feet from the nearest edge of the field and those for the partially tarped were located at 10, 14, 20, 25, 50, and 164 feet. Each sampling mast consisted of a cross-arm at 1.8 m height that held two charcoal sampling tubes at opposite ends of the cross-arm and two battery-powered pumps. The pump flows were set at 2 L/min, but actual flow was measured at the start and end of each sampling period using calibrated rotameters (Gilmont, #3203-20). The sampling masts and meteorological equipment were operated prior to application, during application, and during a number of 4-hour sampling periods up to 48 hours post-application.

The submitted report (Krieger *et al.*, 1998) showed both unadjusted and adjusted MITC concentrations. For the adjustment purposes, it was necessary to determine the "drift window." According to the report, the drift window for each sampling station was determined by fixing the position of each station relative to the points of the compass and then examining the wind direction records for each sampling period to determine what fraction of the sampling time each sampling station was downwind of the treated field. For example, if a sampling station were

positioned due East of the field and the wind blew out of the West during the entire sampling period, then the average concentration of MITC in the air would be the mass of MITC recovered from the charcoal divided by the total volume of air processed (i.e., flow rate x time) during the sampling period. However, if during half the sampling time, the wind direction shifted to the North, for example, then the average MITC concentration in air would be twice that of the previous example, because the volume of air carrying MITC residue to the East station would be half that of the previous example. This document uses the adjusted air concentrations of MITC, which represent downwind MITC air concentrations at various distances from the treated fields. These air concentrations were further adjusted by the author to reflect the fortification recovery of 79.5%.

Fortification recovery study

The study was conducted to determine the recovery of fortified amount of MITC from adsorbent tubes operated under similar conditions to field sample collection. The recovery is used to adjust the amounts of MITC obtained from field samples. Duplicate spikes of 100 ng and 400 ng MITC were made into the intakes of air sampling tubes containing 1 g coconut charcoal (SKC West, Fullerton, CA) by depositing the spikes, while air was flowing at about 2 L/min, onto small polyurethane foam plugs inserted into the tube intakes. The airflow was maintained for about 4 hours using battery-powered pumps (SKC). Air blanks (i.e., no MITC spikes) were also run at the same time.

Analysis and recovery

MITC in the charcoal was eluted using an organic solvent (50:50 v/v ethyl acetate/carbon disulfide), filtered through a 0.45 μm membrane, and determined using nitrogen-phosphorus thermionic gas chromatography by comparing the analyte response with that of standards. The LOQ was determined to be approximately 0.1 $\mu g/m^3$. The recoveries of fortified samples were 79.0% and 80.0% for the spiked amounts of 100 ng and 400 ng, respectively. The average recovery of 79.5% was used to adjust MITC concentrations obtained from the field study.

Results of the study

Off-site, downwind MITC concentrations for each sampling station from the application of metam-sodium by drip irrigation to untarped and partially tarped fields are shown in Table 25. These air concentrations were adjusted to reflect the average recovery of 79.5%. Absorbed dosages were not calculated at this time because the risk assessor has recently changed the No-Observed-Effect level based on a new toxicology study. Currently, MITC concentrations, instead of absorbed dosages, are used to calculate margins of exposure.

Table 25. Average off-site MITC concentrations for each sampling station from the application of metam-sodium by drip irrigation to untarped and partially tarped fields[a].

A. Untarped field

| Distance (ft)[b] | Station[c] | Sampling periods (h) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Application | 4 | 8 | 24 | 36 | 48 |
| | | Adjusted MITC concentrations (ppb) | | | | | |
| 10 | A | 29.5 | 18.8 | 20.5 | 9.3 | 10.8 | 5.0 |
| 14 | B | 49.2 | 15.1 | 11.6 | 14.3 | 11.3 | 7.0 |
| | C | 0.8 | 8.3 | 1.4 | 2.7 | 8.4 | 3.2 |
| | D | 13.6 | 18.7 | 7.9 | 3.9 | 6.5 | 2.0 |
| 20 | E | 12.1 | 56.1 | 26.8 | 24.5 | 70.4 | 5.9 |
| 25 | H | 78.1 | 27.8 | 21.4 | 16.4 | 7.5 | 7.7 |
| 50 | F | 11.7 | 55.5 | 19.0 | 29.4 | 51.7 | 5.6 |
| | I | 34.1 | 23.3 | 21.9 | 18.8 | 8.0 | 7.3 |
| 140 | G | 3.5 | 35.4 | 19.2 | 20.7 | 40.4 | 3.8 |
| 164 | J | 3.7 | 13.3 | 11.3 | 9.3 | 2.2 | 6.0 |

B. Partially tarped field

| Distance (ft)[b] | Station[c] | Sampling periods (h) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Application | 4 | 8 | 24 | 36 | 48 |
| | | MITC concentrations (ppb) | | | | | |
| 10 | O | 0.02 | 16.81 | 13.40 | 0.02 | 0.02 | 0.02 |
| | N | 3.42 | 10.55 | 8.80 | 4.62 | 1.41 | 1.73 |
| 14 | S | 2.43 | 25.98 | 12.92 | 12.94 | 0.40 | 0.02 |
| | T | 10.04 | 46.84 | 35.88 | 5.17 | 3.43 | 1.80 |
| 20 | K | 24.72 | 53.99 | 36.57 | 6.57 | 3.93 | 2.52 |
| | P | 37.52 | 41.05 | 12.94 | 11.87 | 3.00 | 4.60 |
| 50 | L | 40.73 | 62.81 | 21.09 | 5.46 | 4.64 | 1.31 |
| | Q | 43.06 | 35.88 | 12.52 | 9.54 | 2.77 | 6.07 |
| 164 | R | 56.09 | 19.66 | 7.42 | 9.28 | 1.43 | 2.99 |
| | M | 9.58 | 24.96 | 3.24 | 1.79 | 2.69 | 0.02 |

(μg/m3 = ppb x 2.99)

[a] Samples were collected during application (assumed to be 4 hours for untarped field and 2.4 hours for partially tarped field) and a number of 4-hour sampling periods up to 48 hours post-application. MITC concentrations were adjusted to reflect downwind air concentrations by Krieger *et al.* (1998). These values were further adjusted by the author to reflect the average fortification recovery of 79.5%. The data do not represent the time-weighted average MITC concentrations because samples were not collected continuously between those time periods (Personal communication with Dr. Robert I. Krieger, February 25, 2002).

[b] Distance from the nearest edge of field.

[c] Each sampler at each sampling station had a cross arm holding two sampling tubes, one on each end of the arm. The sampling tubes were set at 2 meters apart and 1.8 meters above the ground level.

MITC air concentrations were averaged according to distances of sampling stations from the treated fields, and are shown in Table 26. These MITC concentrations are shown for 1- (during application), 8-, 24-, and 48-hour sampling periods. One-hour MITC concentration is the average of duplicate samples when there was only one sampling station at a specified distance or it is the highest of the average MITC concentration from a station when there are two or more sampling stations at the same distance during application. MITC concentrations for 8-, 24-, and 48-hour sampling periods represent the average MITC concentrations at the same distance for the same sampling period.

MITC concentrations for the range of distances from the treated fields such as 10-50 feet and 140-164 feet for the untarped fields are shown in Table 27. Air concentrations during applications shown as 1-hour exposure were determined for the highest value, mean of averages, and standard deviation whenever they could be calculated. MITC concentrations obtained from the 48-hour sampling period were normalized (amortized) to represent intermediate- and long-term exposures (Table 27). Results are also shown in Tables 17, 18, 19, 20, and 31. Exposure days for workers and residents for intermediate-term off-site exposure to MITC are 23 days in a 120-day period and exposure days for long-term exposure to MITC are 70 days in a 365-day period. Absorbed dosages can be calculated by adjusting for inhalation rates and body weights for adult males and females and children.

Table 26. Off-site MITC concentrations from the application of metam-sodium by drip irrigation to untarped and partially tarped fields[a].

| | | Sampling period (h)[b] | | | |
|---|---|---|---|---|---|
| | | 1 | 8 | 24 | 48 |
| Distance, ft (m) | Sampling station[c] | Adjusted MITC (ppb)[d] | | | |
| A. Untarped field | | | | | |
| 10 (3.0) | A | 29.5 | 20.5 | 9.3 | 5.0 |
| 14 (4.3) | B, C, D | 49.2 | 7.0 | 7.0 | 4.1 |
| 20 (6.1) | E | 12.1 | 26.8 | 24.5 | 5.9 |
| 25 (7.6) | H | 78.1 | 21.4 | 16.4 | 7.7 |
| 50 (15.2) | F, I | 34.1 | 20.5 | 24.1 | 6.5 |
| 140 (42.7) | G | 3.5 | 19.2 | 20.7 | 3.8 |
| 164 (50.0) | J | 3.7 | 11.3 | 9.3 | 6.0 |
| B. Partially tarped field | | | | | |
| 10 (3.0) | O, N | 3.4 | 11.1 | 2.3 | 0.9 |
| 14 (4.3) | S, T | 10.0 | 24.4 | 9.1 | 0.9 |
| 20 (6.1) | K, P | 37.5 | 24.8 | 9.2 | 3.6 |
| 50 (15.2) | L, Q | 43.1 | 16.8 | 7.5 | 3.7 |
| 164 (50.0) | R, M | 56.1 | 5.3 | 5.5 | 1.5 |

[a] The application rate was 319.5 lbs AI/acre. The partially tarped field was covered with 1.5 mm plastic mulch.

[b] One-hour MITC concentration represents the average of duplicate samples when there was only one sampling station at a specified distance or the highest of the average MITC concentration from a station when there are two or more sampling stations at the same distance during application. MITC concentrations for 8-, 24-, and 48-hour sampling periods represent the average MITC concentrations at the same distance for the same sampling period.

[c] Duplicate samples were collected at each sampling station.

[d] MITC concentrations were adjusted to reflect downwind air concentrations by Krieger *et al.* (1998). These values were further adjusted by the author to reflect the average fortification recovery of 79.5%.

Table 27. Exposure of residents to short-, intermediate-, and long-term MITC air concentrations after drip irrigation of metam-sodium to untarped and partially tarped fields[a].

| Distance | | | Exposure time (h) 1[b] | 8[c] | 24[c] | I-term[d] | L-term |
|---|---|---|---|---|---|---|---|
| | | | Adjusted MITC concentrations (ppb) | | | | |
| Untarped field | | | | | | | |
| 10-50 ft | Highest value | | 78.1 | | | | |
| (3.0-15.2 m) | Mean | | 40.6 | 19.2 | 16.3 | 1.1 | 1.1 |
| | STDEV | | 24.8 | 7.3 | 8.1 | 0.3 | 0.3 |
| | Range[e] | Low | 12.1 | 7.0 | 7.0 | 0.8 | 0.8 |
| | | High | 78.1 | 26.8 | 24.5 | 1.5 | 1.5 |
| | Replicates[f] | | 5 | 5 | 5 | 5 | 5 |
| 140-164 ft | Highest value | | 3.7 | | | | |
| (42.7-50.0 m) | Mean | | 3.6 | 15.3 | 15 | 0.9 | 0.9 |
| | STDEV | | N/A | N/A | N/A | N/A | |
| | Range[e] | Low | 3.5 | 11.3 | 9.3 | 0.7 | 0.7 |
| | | High | 3.7 | 19.2 | 20.7 | 1.2 | 1.2 |
| | Replicates[f] | | 2 | 2 | 2 | 2 | 2 |
| B. Partially tarped field | | | | | | | |
| 10-50 ft | Highest value | | 43.1 | | | | |
| (3.0-15.2 m) | Mean | | 23.5 | 19.3 | 7.0 | 0.4 | 0.4 |
| | STDEV | | 19.7 | 6.6 | 3.2 | 0.3 | 0.3 |
| | Range[e] | Low | 3.4 | 11.1 | 2.3 | 0.2 | 0.2 |
| | | High | 43.1 | 24.8 | 9.2 | 0.7 | 0.7 |
| | Replicates[f] | | 4 | 4 | 4 | 4 | 4 |
| 164 feet | Mean | | 56.1 | 5.3 | 5.5 | 0.3 | 0.3 |
| (50 m) | Replicates[f] | | 1 | 1 | 1 | 1 | 1 |

I-term is intermediate-term; L-term is long-term

[a] The application rate was 319 lbs AI/acre. The partially tarped field was covered with 1.5 mm plastic mulch. Downwind MITC concentrations were adjusted by the author to reflect the average fortification recovery of 79.5%.

[b] Combined 1-hour exposures shows the highest MITC or the mean of highest averages from different stations of specified distance during application.

[c] Eight- and 24-hour exposures represent MITC concentrations from 8- and 24-hour sampling periods. These data do not represent the time-weighted average MITC concentrations.

[d] MITC concentrations from the 48-hour sampling periods were normalized (amortized) to reflect 23 exposure days in a 120-day period for intermediate-term exposure and 70 days in a 365-day period for long-term exposure.

[e] Range represents low and high average MITC concentrations from different distances.

[f] MITC concentration for each distance was counted as one replicate.

**C. Exposure of children to MITC**

Children can be exposed to ambient and off-site airborne MITC similar to exposure of adults as previously presented. It is assumed that the exposure scenarios for children are similar to those for adults. Based upon this assumption, the difference between the exposure of adults and children depends on their inhalation rates, body weights, and activity patterns. A correction factor was derived for use in the estimation of exposure of children to MITC from the exposure data of adults.

Based on available information, the ratio of inhalation rates and body weights of six-year-old male children is the highest for resting, light, and moderate activities (U.S. EPA, 1997). A correction factor was derived based on the body weight and inhalation rate for six-year-old children. For six-year-old children, the inhalation rate is 16.74 $m^3$/day and the body weight is 22 kg (U.S. EPA, 1997). This daily inhalation rate takes into account the activity patterns with respect to resting, light, moderate, and heavy activities. The inhalation rate for a 77 kg adult male is 21.4 $m^3$/day (U.S. EPA, 1997). The correction factor is determined to be 2.7 (16.74 $m^3$/day ÷ 22 kg/21.4 $m^3$/day ÷ 77 kg). Short-term air concentrations and estimated average dosages of MITC are shown in Table 28. Intermediate-term air concentrations and estimated average dosages for intermediate- and long-term exposures are shown in Table 29. Exposures of children to short-, intermediate-, and long-term air concentrations obtained from the study sponsored by the MSTF (1999b) were also estimated and are shown in Table 30. Exposures of children to short-, intermediate-, and long-term MITC concentrations from the applications of metam-sodium by drip irrigation to untarped and partially tarped fields are the same as those for adults (Tables 25 to 27).

Table 28. Short-term air concentrations and absorbed daily dosages of MITC from ten studies: Exposure of children.[a]

| | | Method of application/ sampling site | n[b] | Air conc. (TWA) Mean (ppb) | ADD[c] (µg/kg/day) |
|---|---|---|---|---|---|
| B.1[d] | Contra Costa County (CARB, 1993) (Cool air, 43.4-73.8 °F; Cool soil, 53-55 °F) | Soil injection | 1 | 618 | 1388 |
| B.2 | Kern County (CARB, 1994a) | Ambient monitoring | | | |
| | (Warm air & warm soil) | Shafter site | 1 | 1.08 | 2.43 |
| | (Temp. range was not given) | Bakersfield site | 1 | 2.92 | 6.56 |
| | | Lamont site | 1 | 8.3 | 18.9 |
| | | Weed Patch site | 1 | 8.76 | 19.7 |
| B.3[d] | Kern County (CARB, 1994b) (Warm air, 61-92 °F; Warm soil, 79-88 °F) | Soil injection | 3 | 472 | 1058 |
| B.4 | Kern County (Wofford *et al*., 1994) | Fixed-set sprinklers | | | |
| | (Warm air, 77-97 °F) | 5 meters | 5 | 1102 | 2476 |
| | | 75 meters | 5 | 878 | 1974 |
| | | 150 meters | 5 | 468 | 1053 |
| B.5[d] | Madera (Zeneca Inc., 1993b) | Fixed-set sprinklers | | | |
| | (Warm soil, 58-88 °F) | 5 meters | 6 | 186 | 418 |
| | (Warm air, 53-94 °F) | 25 meters | 6 | 171 | 383 |
| | | 125 meters | 6 | 118 | 266 |
| | | 500 meters | 6 | 22.8 | 51.3 |
| B.6[d] | Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F) | Soil injection | 1 | 236 | 529 |
| B.7 | Bakersfield (Seiber *et al*., 1999) | Ambient monitoring | | | |
| | (Summer) | Lamont: houses | 1 | 5.94 | 13.3 |
| | | Lamont: environment | 1 | 2.53 | 5.67 |
| | | Weedpatch: environ. | 1 | 4.76 | 10.7 |
| | | Shafter: houses | 1 | 6.56 | 14.7 |
| | | Shafter: environment | 1 | 7.71 | 17.3 |
| | (Winter) | Lamont: houses | 1 | 1.21 | 2.73 |
| | | Weedpatch: environ. | 1 | 1.64 | 3.67 |
| | | Arvin: houses | 1 | 0.74 | 1.67 |
| | | Arvin: environ. | 1 | 0.27 | 0.59 |
| B.8 | Lompoc (DPR, 2003b) | Ambient monitoring | 1 | 0.25 | 0.57 |

Table 28 (cont.). Short-term air concentrations and absorbed daily dosages of MITC from ten studies: Exposure of children[a]

| | Method of application/ sampling site | n[b] | Air conc. (TWA) Mean (ppb) | ADD[c] (µg/kg/day) |
|---|---|---|---|---|
| B.9[e] Kern County (MSTF, 1999b) | 150 meters | 1 | 101 | 230 |
| (Sprinkler irrigation) | 300 meters | 1 | 52 | 117 |
| | 700 meters | 1 | 31 | 69.2 |
| | 150 meters | 1 | 175 | 396 |
| (Shank injection) | 300 meters | 1 | 106 | 240 |
| | 486 meters | 1 | 84 | 191 |
| B.10 Orange County (Krieger *et al*., 1998) | | | | |
| (untarped field) | 3-15.2 meters | 5 | 16.3 | [f] |
| | 42.7-50 meters | 2 | 15.0 | [f] |
| (partially tarped field) | 3-15.2 meters | 4 | 7.0 | [f] |
| | 50 meters | 1 | 5.5 | [f] |

[a] 1) Mean (arithmetic) air concentrations and ADDs are based on the short-term and downwind (except B.7 and B.8) air monitoring data, e.g., 24-hour-TWA or closest to 24-hour-TWA, except for B.2 and B.6 where air concentration represents the highest, downwind air concentration. The range is not the TWA value. The ADDs represent exposure estimates for six-year old children. The inhalation rate for six-year old children is 16.74 $m^3$/day (U.S. EPA, 1997).
2) The application rates for B.2, B.7, and B.8 were not known because they were ambient air monitoring studies for MITC, and they were not associated with specific metam-sodium applications. Air concentrations and estimated average dosages of MITC from these three studies were not adjusted for the maximum application rate of metam-sodium.

[b] "n" represents numbers of samples (replicates) collected.

[c] ADD (absorbed daily dosage, µg/kg body weight/day) = [µg/$m^3$ (use short-term air concentration) x inhalation rate ($m^3$/h or $m^3$/day)]/[BW]. The average doses for male children are assumed to be similar to those for female children.

[d] The soil was not "sealed" following application, as is currently required. The MITC air concentrations measured during the application of metam-sodium may not be representative of current practices. The study was included in this document to provide historical perspective.

[e] Represent highest downwind MITC concentrations.

[f] Not calculated because the absorbed dose is no longer employed in the MITC risk assessment.

Note: Four studies (B.1, B.3, B.5, and B.6) shown in the shaded area are retained for historical perspective, only. The soil in these studies was not "sealed" following application, as is currently required by the Technical Information Bulletin.

Table 29. Intermediate- and long-term air concentrations and average daily dosages of MITC from ten studies: Exposure of children.[a]

| | | Method of application/ sampling site | n[b] | Air conc. (TWA) Mean (SD) (ppb) | (µg/kg/day) SADD (SD)[c] | AADD (SD)[d] |
|---|---|---|---|---|---|---|
| B.1[e] | Contra Costa County (CARB, 1993) (Cool air, 43.4-73.8 °F; Cool soil, 53-55 °F) | Soil injection | 7 | 246 | 106 | 106 |
| B.2 | Kern County (CARB, 1994a) | Ambient monitoring | | | | |
| | (Warm air & warm soil) | Shafter site | 8 | 0.17 | 0.32 | 0.19 |
| | (Temp. range was not given) | Bakersfield site | 8 | 1.01 | 1.97 | 1.17 |
| | | Lamont site | 8 | 2.85 | 5.54 | 3.29 |
| | | Weed Patch site | 8 | 4.09 | 8.0 | 4.73 |
| B.3[e] | Kern County (CARB, 1994b) (Warm air, 61-92 °F; warm soil, 79-88 °F) | Soil injection | 8 | 229 | 98.8 | 98.82 |
| B.4 | Kern County (Wofford *et al*., 1994) | | | Fixed-set sprinklers | | |
| | (Warm air, 77-97 °F) | 5 meters | 9 | 419 | 180 | 180 |
| | | 75 meters | 9 | 338 | 146 | 146 |
| | | 150 meters | 6 | 322 | 139 | 139 |
| B.5[e] | Madera (Zeneca Inc., 1993b) | Fixed-set sprinklers | | | | |
| | (Warm soil, 58-88 °F) | 5 meters | 13 | 101 | 43.4 | 43.4 |
| | (warm air, 53-94 °F) | 25 meters | 13 | 95.7 | 41.3 | 41.3 |
| | | 125 meters | 13 | 63.8 | 27.5 | 27.5 |
| | | 500 meters | 13 | 13.1 | 5.62 | 5.62 |
| B.6[e] | Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F) | Soil injection | 6 | 81.9 | 35.4 | 35.4 |
| B.7 | Bakersfield (Seiber *et al*., 1999) | Ambient monitoring | | | | |
| | (Summer) | Lamont: houses | 43 | 1.07 (1.40) | 2.08 (2.73) | 1.24 (1.62) |
| | | Lamont: environment | 14 | 0.94 (0.86) | 1.84 (1.67) | 1.08 (1.00) |
| | | Weedpatch: environ. | 12 | 1.39 (1.45) | 2.70 (2.81) | 1.62 (1.67) |
| | | Shafter: houses | 45 | 0.46 (1.07) | 0.89 (2.08) | 0.54 (1.24) |
| | | Shafter: environment | 15 | 0.59 (1.97) | 1.16 (3.83) | 0.68 (2.27) |
| | (Winter) | Lamont: houses | 16 | 0.37 (0.36) | 0.73 (0.70) | 0.43 (0.43) |
| | | Weedpatch: environ. | 8 | 0.50 (0.59) | 0.97 (1.16) | 0.57 (0.70) |
| | | Arvin: houses | 15 | 0.18 (0.21) | 0.35 (0.41) | 0.22 (0.24) |
| | | Arvin: environ. | 6 | 0.13 (0.12) | 0.27 (0.24) | 0.16 (0.14) |
| B.8 | Lompoc (DPR, 2003b) | Ambient monitoring | 1 | 0.0007 | 0.001 | 0.0008 |

Table 29 (cont.). Intermediate- and long-term air concentrations and average daily dosages of MITC from ten studies: Exposure of children.[a]

| | Method of application/ sampling site | Air conc. (TWA) Mean (SD) n[b] | (ppb) | (µg/kg/day) SADD (SD)[c] | AADD (SD)[d] |
|---|---|---|---|---|---|
| B.9[e] Kern County (MSTF, 1999b) | 150 meters | 3 | 55 | 8.68 | 8.68 |
| (Sprinkler irrigation) | 300 meters | 3 | 31 | 5.01 | 5.01 |
| | 700 meters | 3 | 11 | 1.86 | 1.86 |
| | 150 meters | 3 | 67 | 10.7 | 10.7 |
| (Shank injection) | 300 meters | 3 | 39 | 6.18 | 6.18 |
| | 486 meters | 3 | 29 | 4.58 | 4.58 |
| B.10 (Krieger *et al*., 1998) | 3-15.2 meters | 5 | 5.84 | 1.1 ppb[f] | 1.1 ppb[f] |
| (untarped field) | 42.7-50 meters | 2 | 4.90 | 0.9 ppb[f] | 0.9 ppb[f] |
| (partially tarped field) | 3-15.2 meters | 4 | 2.28 | 0.4 ppb[f] | 0.4 ppb[f] |
| | 50 meters | 1 | 1.5 | 0.3 ppb[f] | 0.3 ppb |

[a] 1). Mean (arithmetic) air concentrations and SADDs are based on the intermediate-term and downwind (except B.7 and B.8) air monitoring data, e.g., sample collection times were 53 hours (B.1), 240 hours (B.2), 64 hours (B.3), and 74 hours (B.4). The range is not the TWA value. The SADDs represent exposure estimates for six-year old children. The inhalation rate for six-year old children is 16.74 $m^3$/day (U.S. EPA, 1997).
2). The application rates for B.2, B.7, and B.8 were not known because they were ambient air monitoring studies for MITC, and they were not associated with metam-sodium applications. Air concentrations and estimated average dosages of MITC were not adjusted for the maximum application rate of metam-sodium. The average doses for male children are assumed to be similar to those for female children.

[b] "n" represents numbers of samples (replicates) collected.

[c] SADD (seasonal average daily dosage, µg/kg body weight/day) = (ADD x Exposure days in a time period or season) ÷ Days in a time period or season. SADD was calculated based on 23 exposure days in a 120-day season (Haskell, 1994) for exposure to off-site MITC and 78 exposure days in a 90-day period for exposure to ambient MITC (Powell, 1999).

[d] AADD (annual average daily dosage, µg/kg body weight/day) = (ADD x Exposure days in a year) ÷ 365 days/year. AADD was calculated based on 70 exposure days in a year (or 23 x 365/120) (Haskell, 1994) for exposure to off-site MITC and 188 exposure days in a year (365 days) for exposure to ambient MITC (Powell, 1999).

[e] The soil was not "sealed" following application, as is currently required. The MITC air concentrations measured during the application of metam-sodium may not be representative of current practices. The study was included in this document to provide historical perspective.

[f] shown as normalized (amortized) MITC air concentrations to reflect workdays per season or per year.

Note: Four studies (B.1, B.3, B.5, and B.6) shown in the shaded area are retained for historical perspective, only. The soil in these studies was not "sealed" following application, as is currently required by the Technical Information Bulletin.

Table 30. Exposure of children to off-site MITC generated from the application of metam-sodium.[a]

1. Sprinkler irrigation

| | | Short-term exposure | | | | Intermediate- or long-term exposure | | | |
|---|---|---|---|---|---|---|---|---|---|
| Distance (m) | Sampling station | | MITC (TWA) (ppb) | ADD[b] (μg/kg/day) | Sampling station | | MITC (TWA) Days 1-4 | (μg/kg/day) SADD[c] | AADD[d] |
| 150 | D | Low | 30 | 67.7 | D | Low | 50 | 21.7 | 21.7 |
| | A | High | 101 | 230 | A | High | 63 | 27.4 | 27.4 |
| | | | | | | Mean | 55 | 23.8 | 23.8 |
| 300 | C | Low | 8 | 17.5 | C | Low | 27 | 12.0 | 12.0 |
| | C | High | 52 | 117 | A | High | 35 | 15.0 | 15.0 |
| | | | | | | Mean | 31 | 13.7 | 13.7 |
| 700 | C | Low | 3.6 | 8.37 | C | Low | 8.3 | 3.65 | 3.65 |
| | A | High | 31 | 69.2 | A | High | 14 | 6.27 | 6.27 |
| | | | | | | Mean | 11 | 5.10 | 5.10 |
| 970 (upwind) | A | Low | 0.08 | 0.18 | A | Low | 2 | 0.86 | 0.86 |
| | B | High | 12.7 | 28.8 | B | High | 4.1 | 1.79 | 1.79 |

2. Shank injection

| | | Short-term exposure | | | | Intermediate- or long-term exposure | | | |
|---|---|---|---|---|---|---|---|---|---|
| Distance (m) | Sampling station | | MITC (TWA) (ppb) | ADD[b] (μg/kg/day) | Sampling station | | MITC (TWA) Days 1-4 | (μg/kg/day) SADD[c] | AADD[d] |
| 150 | D | Low | 5.4 | 12.2 | B | Low | 51 | 22.0 | 22.0 |
| | A | High | 175 | 396 | A | High | 94 | 41.0 | 41.0 |
| | | | | | | Mean | 67 | 29.3 | 29.3 |
| 300 | C | Low | 5.4 | 12.2 | C | Low | 29 | 12.5 | 12.5 |
| | A | High | 106 | 240 | A | High | 56 | 24.4 | 24.4 |
| | | | | | | Mean | 39 | 16.9 | 16.9 |
| 486 | C | Low | 6 | 13.7 | C | Low | 20 | 8.75 | 8.75 |
| | A | High | 84 | 191 | A | High | 39 | 16.9 | 16.9 |
| | | | | | | Mean | 29 | 12.5 | 12.5 |
| 837 (upwind) | B | Low | 4 | 9.13 | A | Low | 33 | 14.2 | 14.2 |
| | B | High | 106 | 242 | B | High | 51 | 22.0 | 22.0 |

[a] MSTF, 1999b.

[b] ADD (absorbed daily dosage) = [$\mu g/m^3$ (short-term MITC) x inhalation rate ($m^3$/day)]/[BW]. Factors used in the calculations were: body weight = 22 kg, inhalation rate = 16.74 $m^3$/day.

[c] SADD (seasonal average daily dosage) = (ADD x Exposure days/120 days) ÷ 120 days/season. SADD was calculated based on 23 exposure days in a 120-day season (Haskell, 1994) for exposure to off-site MITC.

[d] AADD (annual average daily dosage) = (ADD x Exposure days in a year) ÷ 365 days/year. AADD was calculated based on 70 exposure days in a year (Haskell, 1994) for exposure to off-site MITC.

Short-term (1- and 8-hour) MITC air concentrations for residents

Short-term MITC air concentrations are estimated for 1- and 8-hour exposure periods by using data obtained from the studies shown in this document (B.1-B.10). Exposures for the short-term exposure period of 1 or 8 hours are intended for use in the risk assessment of MITC for acute effects because the acute NOELs for MITC relate directly only to 1- or 8-hour exposures. The criteria used in the determination of these MITC air concentrations are shown in Table 8. Exposures of residents to short-term MITC air concentrations are shown in Table 31.

Table 31. Exposure of residents to short-term air concentrations of MITC: Off-site and ambient air monitoring studies.

| Location | Method of application/ sampling site | Air concentrations of MITC (ppb) 1-hour[a] | 8-hour[b] | Notes |
|---|---|---|---|---|
| B.1[c] Contra Costa County (CARB, 1993) (Cool air, 43.4-73.8 °F; Cool soil, 53-55 °F) | Soil injection | 646 | 646 | 625-min. sampling time |
| B.2 Kern County (CARB, 1994a) | Ambient monitoring | | | |
| (Warm air & warm soil) | Shafter site | 1.1 | 1.1 | 1380-min. sampling time |
| (Temp. range was not given) | Bakersfield site | 2.9 | 2.9 | 1365-min. sampling time |
| | Lamont site | 8.3 | 8.3 | 1370-min. sampling time |
| | Weed Patch site | 8.8 | 8.8 | 1370-min. sampling time |
| B.3[c] Kern County (CARB, 1994b) (Warm air, 61-92 °F; Warm soil, 79-88 °F) | Soil injection | 827 | 827 | 785-min. sampling time |
| B.4 Kern County (Wofford *et al*., 1994) | Fixed-set sprinklers | | | |
| (Warm air, 77-97 °F) | 5 meters | 2853 | 2321[d] | 6&1.5-hour sampling times |
| | 75 meters | 2813 | 2348[d] | 6&1.5-hour sampling times |
| | 150 meters | 1760 | 1534[d] | 6&1.5-hour sampling times |
| B.5[c] Madera (Zeneca, 1993b) | Fixed-set sprinklers | | | |
| (Warm soil, 58-88 °F) | 5 meters | 1255 | 811[d] | 4&4-hour sampling times |
| (Warm air, 53-94 °F) | 25 meters | 1043 | 701[d] | 4&4-hour sampling times |
| | 125 meters | 762 | 513[d] | 4&4-hour sampling times |
| | 500 meters | 163 | 106[d] | 4&4-hour sampling times |
| B.6[c] Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F) | Soil injection | 236 | 236 | 760-min. sampling time |
| B.7 Bakersfield (Seiber *et al*., 1999) | Ambient monitoring | | | |
| (Summer) | Lamont: houses | 9.7 | 9.7 | Indoor-PM MITC |
| | Lamont: env. | 5.0 | 5.0 | Outdoor-PM MITC |
| | Weedpatch: env. | 9.4 | 9.4 | Outdoor-PM MITC |
| | Shafter: houses | 13.1 | 13.1 | Indoor-AM MITC |
| | Shafter: env. | 14.6 | 14.6 | Outdoor-AM MITC |
| (Winter) | Lamont: houses | 1.9 | 1.9 | Outdoor-AM MITC |
| | Weedpatch: env. | 1.7 | 1.7 | Outdoor-PM MITC |
| | Arvin: houses | 1.4 | 1.4 | Outdoor-AM MITC |
| | Arvin: environ. | 0.3 | 0.3 | Outdoor-AM/PM MITC |
| B.8 Lompoc (DPR, 2003b) | Ambient monitoring | 0.3 | 0.3 | Shown as the 24-hour TWA |

Table 31(cont.). Exposure of residents to short-term air concentrations of MITC: Off-site and ambient air monitoring studies.

| Location | Method of application/ sampling station | Air concentrations of MITC (ppb) 1-hour[a] | 8-hour[f] |
|---|---|---|---|
| B.9 Bakersfield (MSTF, 1999b)[e] | Sprinkler irrigation | | |
| | A 150 meters | 234 | 195 |
| | B 150 meters | 275 | 191 |
| | D 150 meters | 281 | 193 |
| | A 300 meters | 148 | 133 |
| | B 300 meters | 200 | 124 |
| | C 300 meters | 194 | 133 |
| | A 700 meters | 99 | 90 |
| | B 700 meters | 63 | 53 |
| | C 700 meters | 50 | 31 |
| | A 970 meters | 15 | 8.3 |
| | B 970 meters | 41 | 32 |
| | Shank injection | | |
| | A 150 meters | 281 | 244 |
| | B 150 meters | 131 | 88 |
| | D 150 meters | 144 | 141 |
| | A 300 meters | 216 | 151 |
| | B 300 meters | 101 | 74 |
| | C 300 meters | 67 | 59 |
| | A 486 meters | 199 | 123 |
| | B 486 meters | 109 | 67 |
| | C 486 meters | 39 | 33 |
| | A 837 meters | 43 | 38 |
| | B 837 meters | 242 | 149 |
| B.10 Orange County (Krieger *et al*., 1998) | | | |
| A. Untarped field | 10-50 feet | 78.1[g] | 19.2[h] |
| | 140-164 feet | 3.7[g] | 15.3[h] |
| B. Partially tarped field | 10-50 feet | 43.1[g] | 19.3[h] |
| | 164 feet | 56.1[g] | 5.3[h] |

[a] 1-hour MITC air concentrations represent the highest values.

[b] If same values are shown as in ([a]), they represent the highest MITC concentrations.

[c] The soil was not "sealed" following application, as is currently required. The MITC air concentrations measured during the application of metam-sodium may not be representative of current practices. The study was included in this document to provide historical perspective.

[d] Represent the time-weighted average MITC concentrations of two consecutive samples.

[e] MITC concentrations may not represent downwind MITC; because the wind directions changed during the study.

[f] Approximately the 8-hour TWA of two consecutive samples.

[g] Represent the highest MITC concentration during application (see Table 27, page 66).

[h] Represent the mean MITC concentration for 8-hour sampling period (see Table 27, page 66).

Note: Four studies (B.1, B.3, B.5, and B.6) shown in the shaded area are retained for historical perspective, only. The soil in these studies was not "sealed" following application, as is currently required by the Technical Information Bulletin.

**D. The use of metam-sodium for treating sewer systems**

In 1999, two metam-sodium containing products, Sanafoam Vaporooter™ II and SeweRout™ were used to destroy infiltrating roots in sewer systems (DPR, 1999d). The total amount of Sanafoam Vaporooter™ II sold in 1999 (DPR, 1999d) was about 0.08% of the total reported use of metam-sodium in the same year (DPR, 2000b). The total amount of SeweRout™ sold in 1999 (DPR, 1999d) was about 0.01% of the reported use of metam-sodium in the same year (DPR, 2000b).

The basic method of treatment of these two products is to apply a 1% water solution or foam to an isolated section of the sewer system for an hour. The metam-sodium is contained within the plumbing system being treated and should not pose an exposure problem, provided the system has been adequately isolated (Donahue, 1993). At the end of the treatment time, the treating solution is released into the main sewer system and the treated system flushed with water. It is anticipated that MITC will be formed during the treatment process. MITC may be in air spaces of the plumbing during treatment or in air spaces connecting with the treatment area. Exposure may occur if workers accidentally enter in these areas. Typically, sewer workers are aware of the potential for dangerous levels of various gases that may be present in the confined areas they work in and around. The use of these two specialized products does not appear to pose any unusual worker exposure problems (Donahue, 1993). However, accidental exposure of homeowners or workers to MITC can occur if the sewer system fails or there is a leak in the system.

## EXPOSURE APPRAISAL

This document emphasizes exposures of persons in California to MITC generated from the use of metam-sodium in agriculture. Even though some other pesticides, such as dazomet and metam-potassium, can produce MITC, the amount is insignificant compared to MITC generated from the use of metam-sodium.

Default physiologic factors employed in the calculation, e.g., body weights and inhalation rates were adopted from the current Exposure Factors Handbook of the United States Environmental Protection Agency to maintain consistency. The work time per day (duration of exposure) and workdays or exposure days per season or year (frequency of exposure) were estimated from available information. A large-scale survey for duration and frequency of exposure is not feasible at this time.

Two worker exposure studies were conducted to determine exposure levels of handlers to MITC during the applications of metam-sodium using different methods of application. The study sponsored by the MSTF (1999a) was conducted in accordance with the current TIB, *Guidelines for All Application Methods for Metam-Sodium in California*. Silica gel drying tubes were used in these studies, but were not analyzed for MITC. It is possible that MITC air concentrations could be underestimated as evidenced from the study conducted by Wofford *et al.* (1994). Another study sponsored by the MSTF (MSTF, 2001) was conducted in Kern County, California. Before the initiation of the study, it was determined that silica gel drying tube was not necessary.

Two other studies are presented in this document for historical purposes, only. These studies were conducted in Arizona (A.1; ICI America Inc., 1992) and Washington (A.2; Zeneca Inc., 1993a). While exposure values were calculated, neither of these studies followed the current TIB guidelines. These studies represent extreme case exposure scenarios and may not be representative of legal application methods.

Exposure of handlers to MITC employing other application methods, such as injection blades, fertilizer wheels, plows, disks, check flood (basin), furrow and border chemigation, could not be estimated because field studies using these methods are unavailable. The available studies could not be used as a surrogate because degradation profiles of metam-sodium employing different application methods may be affected by cultivation practices, amount of water used, and environmental conditions.

Ambient and application site (off-site) air concentrations of MITC and the estimated dosages for short-, intermediate-, and long-term exposures were obtained from six studies. Silica gel drying tubes were used in one of these studies (Wofford *et al*., 1994). MITC in this portion of the sampling train was analyzed in the study conducted by Wofford *et al*. (1994). In this study, silica gel tubes were found to retain MITC, ranging from 58 to 100% for one sampling interval and 0 to 4% for another sampling interval. There is some uncertainty concerning the MITC absorption efficiency of silica gel drying tubes. These drying tubes were recommended in the standard operating procedure of Zeneca Inc. There is the possibility that those MITC data obtained from studies that did not analyze silica gel drying tubes for MITC might underestimate exposures.

Off-site air concentrations obtained from the study conducted by Wofford *et al*. (1994) were significantly higher than those from Zeneca Inc. (1993b) for applications of metam-sodium when fixed-set sprinklers were used. Information provided to DPR during the preparation of this report indicates the potential of an inversion during the period of the application in the study conducted by Wofford *et al*. (1994). The presence of an inversion could result in an overestimation of exposure. However, the ability to determine whether an inversion was present during the application cannot be made. Even so, because sprinkler applications are still allowed at night, this study appears to be representative of current practices (Barry and Johnson, 2001). MITC concentrations obtained from the study sponsored by the MSTF (1999b) are similar to those obtained from the study conducted by Zeneca Inc. (1993b). However, MITC data obtained from the study sponsored by the MSTF likely underestimated the exposure because evidence indicated that not all sampling stations were located in the downwind direction. Four other studies are presented in this document for historical purposes, only. These studies were conducted by CARB (B.1 (off-site); CARB, 1993, B.3 (off-site); CARB, 1994b, Zeneca Inc. (B.5 (off-site); Zeneca, 1993b), and B.6 (off-site); CARB, 1997). While exposure values were calculated, none of these studies followed the current TIB guidelines where the soil in these studies was not "sealed" following application, as is currently required. These studies represent extreme case exposure scenarios and may not be representative of legal application methods. Characterizing exposure of residents to MITC cannot be made with high confidence because of limited data and replicates in the aforementioned studies.

Extrapolation of exposure from a short monitoring period to a full workday or 8 hours may over- or underestimate exposure. Short-term (e.g., 1- or 8-hour) MITC concentrations may be underestimated if they are taken from a long sampling period, e.g., 10 hours or longer. In this case, the peak MITC concentration during that sampling period is not known. Consequently, the degree of underestimation is not known.

*Acknowledgment:*

For consistency in the preparation of a risk assessment document, the following sections were provided by Drs. Andrew L. Rubin and Earl F. Meierhenry, Staff Toxicologists, Toxicology Branch: Physical and chemical properties, DPR and U.S. EPA regulatory history, dermal toxicity/eye irritation, animal metabolism, and a portion of usage and formulations/label precautions.

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