EVALUATION OF METHYL ISOTHIOCYANATE AS A TOXIC AIR CONTAMINANT

Part B—Exposure Assessment

California Environmental Protection Agency
Sacramento, California

August 2002

TAC-2002-01B

State of California
Department of Pesticide Regulation

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Evaluation of
Methyl Isothiocyanate
As a Toxic Air Contaminant

Part B
Public Exposure to Airborne Methyl Isothiocyanate
in California

HS-1704

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July 25, 2000
Revision No. 1 August 14, 2000
Revision No. 2 August 17, 2000
Revision No. 3 January 9, 2002

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SUMMARY

Methyl isothiocyanate (MITC) has been used extensively in California to control weeds, soil-borne diseases, and nematodes in soil. MITC is the major degradate of metam-sodium after soil application. MITC is an active agent for pest control purposes. Currently, there are only two active registrations of MITC products in California. Total reported use in 1999 was 620 pounds. There was no reported use in 1996. The annual average amount of MITC produced from metam-sodium (1995-1999) was about 9.2 million pounds. Dazomet can produce MITC. From 1990 through 1999, the annual average illness/injury cases classified as definitely, probably, and possibly attributed to exposure to metam-sodium/MITC were 6.9, 25.2, and 6.9, respectively.

Residents/bystanders can be exposed to ambient or off-site MITC from nearby fumigated fields. Studies conducted or sponsored by California Air Resources Board, Zeneca Inc., University of Nevada, the Metam-Sodium Task Force, and the Department of Pesticide Regulation determined potential exposure levels of residents/bystanders to ambient or off-site MITC residues. There was a wide range of exposure of residents/bystanders to ambient or off-site MITC residues depending on distances from application sites, wind directions, methods of application, and application rates of metam-sodium. The mean short-term (24- or closest to 24-hour) time-weighted average (TWA) MITC concentrations ranged from 0.08 to 1,102 ppb and the absorbed daily dosage (ADD) of adult males ranged from 0.21 to 917 μg/kg body weight/day. One- and 8-hour MITC air concentrations were also estimated. The mean moderate-term TWA MITC concentrations ranged from 0.0007 to 419 ppb and the seasonal average daily dosage (SADD) of adult males ranged from 0.0005 to 66.8 μg/kg body weight/day. The ADD of six-year-old children ranged from 0.57 to 2,476 μg/kg body weight/day and the SADD ranged from 0.001 to 180 μg/kg body weight/day. 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 toxic effects in rats. This report was prepared as part of the Department's risk assessment process for MITC.

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 of Pesticide Regulation (DPR)'s risk assessment process. It will also be used as a basis for developing mitigation proposals if exposures to MITC are found to cause excessive risks.

The exposure estimates for residents/bystanders to MITC were obtained from monitoring ambient air in residential areas and off-site air during and after soil applications of metam-sodium. In addition to exposure estimates, presentations of other properties of MITC are 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, formulation/label precautions, usage, illnesses/injuries, dermal toxicity and eye irritation, dermal/inhalation absorption, and animal metabolism.

On August 14, 2000, this MITC exposure document (Part B, July 25, 2000) was revised (Revision No. 1) as follows: a) Page 41, E. Short-term MITC air concentrations: Summary (Table). Ranges of sampling periods were used instead of multiple time points. Criteria were changed for 1-hour (1. Short-sampling time) and 8-hour MITC concentrations (2. Moderate sampling time); b) Pages 42-43, "Notes" (Tables 18 and 19). Sampling times and replicates are indicated when they are applicable. More footnotes were added to these Tables; c) Page 42, A.3 Bakersfield, California. MITC levels were recalculated and shown as the average (Standard Deviation).

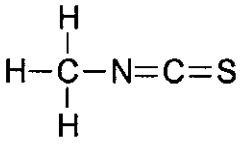
It was found that MITC air concentrations in A.3 Bakersfield, California (Page 42, Table 18) were inadvertently added to this Table. On August 17, 2000, air concentrations under A.3 and related footnotes were removed from this Table (Revision No. 2) because this section is not needed for this document.

On January 8, 2002, this MITC exposure document (Part B, August 17, 2000) was revised (Revision No. 3) as follows: a) Page 10, paragraph 1 - Four studies are included in this document to provide historical perspective. This revision reflects comments from the Metam-Sodium Task Force (MSTF); b) Pages 10 (paragraph 2) and 41 (paragraph 2) – These two paragraphs indicate that the ability to determine whether an inversion was present during the application of metam-sodium in the study conducted by Wofford *et al.* (1994) could not be made; c) "Metam-sodium" is used in front of Vapam® as suggested by the MSTF; d) Summary, paragraph 1 and Illness/Injury Data, paragraph 1 - The indicated illness cases were attributed to exposure to metam-sodium/MITC. Revised the average illness/injury data; e) Usage - Updated the usage of metam-sodium and MITC to show data from 1995 to 1999. Deleted a sentence, "As a soil fumigant, it may be mixed with 1,3-dichloropropene (Paragraph 1)" and replaced "the two products" with "dazomet (paragraph 3)"; f) Illness/Injury Data - Added illness/injury data from 1997 to 1999 to this section; g) Exposure Assessment - MITC data obtained from two worker exposure studies and related information were deleted because the Toxic Air Contaminant process does not consider worker exposure data. Added footnotes for studies A.1, A.3, A.5, and

A.6 in Tables 8a, 8b, 9a, 9b, 14, and 15 to indicate that 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; h) Exposure Appraisal, paragraph 2 - A statement shown in (a) was included and paragraph 5 - Added a statement, "MITC concentrations in air obtained from the study sponsored by the MSTF are likely underestimated because evidence indicated that not all sampling stations were located in the downwind direction."

PHYSICAL AND CHEMICAL PROPERTIES

(Degussa Corporation, 1988)

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 °C
10.	Odor:	Pungent, similar to horseradish
11.	Color:	Yellowish
12.	Boiling point:	119 °C
13.	Melting point:	34 °C
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 °C.
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 °C (Tomlin, 1997)
18.	Octanol/Water partition coefficient:	19
19.	Corrosion characteristics:	Corrosive against 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.

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, 2001).

Label Precautions

The two MITC products are Toxicity Category I pesticides that have a signal word "DANGER." The products are restricted use pesticides. 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 Safety and Health Administration and the National Institute for Occupational Safety and Health; wear goggles, safety glasses or face shield, protective clothing and rubber gloves.

USAGE

Methyl isothiocyanate is a general biocide used to control weeds, nematodes, and soil and wood fungi. As a wood preservative pesticide, MITC is poured in small holes bored into utility poles. MITC is also the active principle of the soil fumigant metam-sodium and dazomet.

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 MITC from metam-sodium 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).

Production of MITC from dazomet is negligible compared to that generated from metam-sodium. In 1997, the amount of use of dazomet in agriculture was 13,305 lb a.i. (DPR, 1999b). Therefore, exposure of workers and residents/bystanders to MITC generated from dazomet is insignificant.

The estimated quantities of MITC from the use of MITC products and MITC generated from the use of metam-sodium in 1995 to 1999 in California are shown in Table 1.

Table 1. Use and estimated total production of MITC in California between 1995-1999.

		Amount of MITC (million pounds, lbs)		
Year	Use of metam-sodium[a]	MITC generated from metam-sodium[b]	MITC products	Total MITC
1995 (DPR, 1996a)	15.3	9.2	0.10×10^{-3}	9.2
1996 (DPR, 1999a)	15.2	9.1	0.00	9.1
1997 (DPR, 1999b)	15.0	9.0	0.40×10^{-3}	9.0
1998 (DPR, 2000a)	14.0	8.4	0.22×10^{-3}	8.4
1999 (DPR, 2000b)	17.3	10.4	0.62×10^{-3}	10.4
Average (1995-1999)	15.4	9.2	0.27×10^{-3}	9.2

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

ILLNESS/INJURY DATA

There were 390 illnesses/injuries attributed to exposure to metam-sodium/MITC reported in California from 1990 to 1999 (Mehler, 2000). From 1990 through 1999, the annual average illness/injury cases classified as definitely, probably, and possibly attributed to exposure to metam-sodium/MITC were 6.9, 25.2, and 6.9, respectively (Table 2). The majority of illness/injury cases from 1990 to 1999 occurred to workers during field fumigation and to residents/bystanders following off-site movement of MITC (usually 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. It was assumed that the majority of illnesses/injuries associated with metam-sodium were caused by exposure to MITC because it is the major degradate of metam-sodium after application to soil.

Table 2. Case reports received by the California Pesticide Illness Surveillance Program in which health effects were attributed to exposure to metam-sodium/MITC (1990-1999): Reported 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
Average	6.9	25.2	6.9	39.0

[a] In 1993, there were two illnesses/injuries attributed to exposure to metam-sodium/MITC in combination with other pesticides. Thus, there were altogether 392 illness/injury cases from 1990 to 1999. 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 (1990-1999): Reported according to activities at the time of exposure.[a]

Activity	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	Total
Loader	0	1	1	3	3	3	3	5	0	0	19
Applicator	1	0	0	2	0	1	3	2	2	0	11
Fumigation, field	14	7	1	1	3	0	0	5	1	2	34
Drift: Occupational	2	0	0	0	0	0	2	0	0	8	12
Non-occup.	0	0	11	11	0	40	48	0	1	167	278
All others	3	5	5	1	4	4	0	8	0	6	36
Total	20	13	18	18	10	48	56	20	4	183	390

[a] In 1993, there were two illnesses/injuries attributed to exposure to metam-sodium/MITC in combination with other pesticides. Thus, there were altogether 392 illness/injury cases from 1990 to 1999. 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 (1990-1999): Reported 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
Average	26.8	6.9	5.0	3.0	39.0

[a] In 1993, there were two illnesses/injuries attributed to exposure to metam-sodium/MITC in combination with other pesticides. Thus, there were altogether 392 illness/injury cases from 1990 to 1999. 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: eyes - 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% a.i.). Each animal was exposed to 0.5 mL technical MITC (heated to 40 °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, 1988a).

A primary eye irritation study was conducted in one male and two female New Zealand white rabbits using technical MITC (97% a.i.). Each animal was exposed to 0.1 mL technical MITC (heated to 40 °C to liquefy). The results showed that MITC caused a primary eye irritation in rabbits under conditions specified in this study (Degussa Corporation, 1988b). 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 was not available. It is assumed that the dermal dose of MITC vapor is very low compared to the systemic dose received by inhalation. Exposure of workers and residents/bystanders to MITC vapor were estimated by monitoring ambient air concentrations. Monitoring of dermal exposure to MITC is extremely difficult, if not impossible. Registrants did not conduct a dermal exposure study for MITC during and after application of MITC or metam-sodium products.

There was no inhalation uptake/absorption study of MITC. The absorbed dose of MITC has to be 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%. The default inhalation uptake 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 CO_2), and Viles' reagent (to trap carbonyl sulphide (COS) and CS_2). Following doses of MITC, the radioactivity was principally eliminated in urine 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 a volatile metabolite was eliminated in exhaled air. This metabolite was retained in the 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).

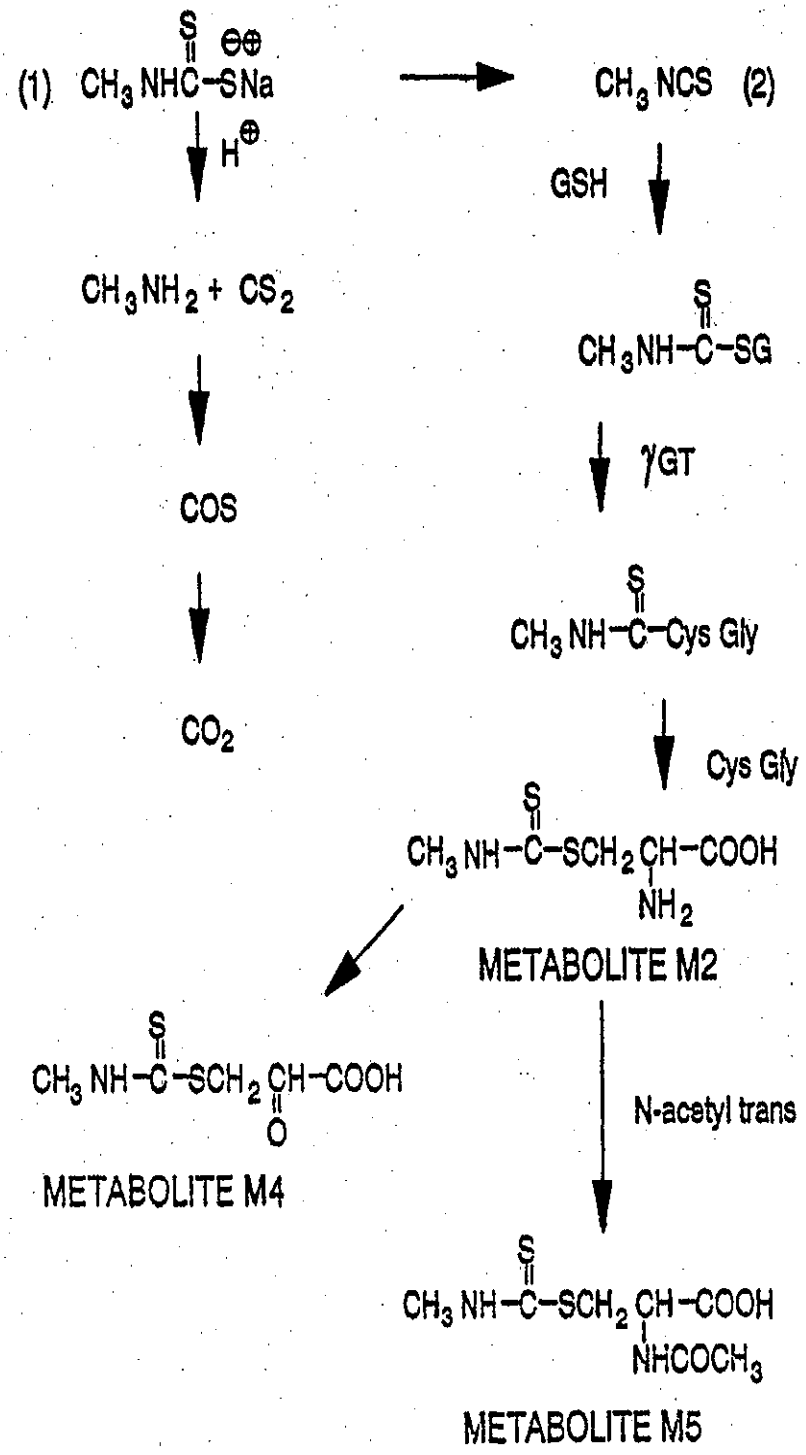
Table 5. Excretion and retention of radioactivity (% of dose) following metam-sodium or MITC oral gavage to rats (n = 5 per dose).

	% Dose							
	Metam-sodium				MITC			
	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)	0.45	1.26	24.53	24.04	0.95	1.51	0.72	1.67
Expired air (CO_2)	19.56	18.13	7.20	5.53	16.08	14.88	7.32	7.23
Expired air (COS & CS_2)	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

Tissue content was highest in the thyroid on a μg/g basis at 168 hours. Kidneys and liver 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, 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 was identified as N-acetyl-S-(N-methylthiocarbamoyl)-L-cysteine. The other metabolite 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).



EXPOSURE ASSESSMENT

The exposure data from nine studies (A.1-A.9) for ambient or off-site MITC were evaluated, four of which were conducted by the California Air Resources Board (CARB), two by the Department of Pesticide Regulation (DPR) (Wofford *et al.*, 1994; DPR, 1999d), and one each by the University of Nevada (Seiber *et al.*, 1999), Zeneca Inc. (1993), and MSTF (1999). The current metam-sodium technical information bulletin (TIB), which is part of the label when metam-sodium is used in California, specifically requires the soil to be "sealed" immediately following application to minimize off-site movement of odors. During the four studies of A.1 (CARB, 1993), A.3 (CARB, 1994b), A.5 (Zeneca, 1993), and A.6 (CARB, 1997) the soil was not "sealed" following application, as is currently required. Therefore, the air concentrations measured during these applications may not be representative of current practices. These studies were included in this report to provide historical perspective. Human exposure was calculated from A.2 (CARB, 1994a), A.4 (Wofford *et al.*, 1994), A.7 (Seiber *et al.*, 1999), A.8 (DPR, 1999d), and A.9 (MSTF, 1999).

Scientists at DPR believe that the study (A.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 exposure estimates reported in this document, whenever they are appropriate, are shown as parts per billion (ppb), an absorbed daily dosage (ADD) or a seasonal average daily dosage (SADD). Exposure data were adjusted for field fortification recoveries and the maximum metam-sodium application (label) rate of 318 lb a.i. 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 non-detectable (ND), unless mentioned otherwise in this document. Several default physiologic and other factors are needed for the calculation of MITC exposures of residents/bystanders. These principal default factors are listed in Table 6 and below.

Dermal exposure or dermal uptake of MITC could not be quantitatively estimated at this time because of lack of a supporting data.

Calculation procedures and some default factors:

1. MITC: air concentration ($\mu g/m^3$) = [(correction factor) x MW x (ppb)]/24.45
   or $\mu g/m^3$ = corrected ppb x 2.99; ppb = corrected $\mu g/m^3$ x 0.334. (MITC MW = 73.1)
   Where correction factor = [(318 lb a.i./A (max.)]/[appl. rate (lb a.i./A)] x [% observed recovery]$^{-1}$
   (Note: One gram mole of an ideal gas or vapor occupies a volume of 24.45 liters at 25 °C and 760 mm Hg pressure.)
2. Short-term exposure:
   ADD (μg/kg body weight/day) = [$\mu g/m^3$ (use short-term air concentration) x inhalation rate (m^3/day)]/[BW].
3. Moderate-term exposure:
   SADD (μg/kg body weight/day) = ADD* x Exposure days in a time period or season / Days in a time period or season
   * Use moderate-term air concentrations and daily inhalation rates. These inhalation rates take into account the activity patterns in respect to resting, light, moderate, and heavy activities.

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

Exposure	Person	BW (kg)	Inhalation rate	Exposure days	Reference
A. Residents/bystanders (adults)					
Short-term	Adult male	77	21.4 m^3/day	Daily	U.S. EPA, 1997 (T. 7-4, 5-18)
	Adult female	62	11.8 m^3/day	Daily	U.S. EPA, 1997 (T. 7-5, 5-18)
Mod.-term	Adult male	77	21.4 m^3/day	23/120[a]	U.S. EPA, 1997 (T. 7-4, 5-18)
	Adult female	62	11.8 m^3/day	23/120[a]	U.S. EPA, 1997 (T. 7-4, 5-18)
B. Residents/bystanders (children)					
Short-term	Children	22	16.74 m^3/day	Daily	U.S. EPA, 1997 (T. 7-6, 5-18)
Mod.-term	Children	22	16.74 m^3/day	23/120[a]	U.S. EPA, 1997 (T. 7-6, 5-18)

[a] For moderate-term exposure, frequency of exposure is 23 days in a 120-day period. The exposure days are applicable to residents, who are exposed to MITC in the vicinity of treated fields (from application site monitoring). The average frequency of exposure of residents to ambient MITC (from ambient air monitoring studies) is 78 days in a 90-day period (Powell, 1999). The number of workdays per season (23/120) for handlers was based on data from Haskell (1994). Handlers were assumed to work 15 days for a 15-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 and bystanders 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.

Bergeson&Campbell (1999) suggested eight exposure days per season or year for workers and residents (Bergeson&Campbell, 1999). However, Bergeson&Campbell did not provide adequate background information to substantiate the suggested exposure days. An example of exposure calculation is shown in Table 7.

Table 7. Example of exposure calculation[a] (Air monitoring in Kern County, C94-046A, CARB, 1997).

Downwind sample ID		Time (min)	MITC (ppb)	Appln. rate (lb a.i./A)	Corrected for appln. rate (ppb)	Recovery (%)	Corrected for recovery (ppb)	µg/m³	TWA[b] µg/m³	MIR (m³/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				
		760	84	155	172	73	236	707			Exposure (µg/day)	Exposure frequency	SADD (µg/kg/day)
		675	2.7	155	5.54	73	7.59	22.7					
		770	57	155	117	73	160	480	245	21.4	5,244	23/120	13.05
		600	1.1	155	2.26	73	3.09	9.26					
		795	6.7	155	13.8	73	18.8	56.4					
Range		370	0.21	155	0.43	73	0.59	1.77		21.4	37.8	23/120	0.09
		760	84	155	172	73	236	707		21.4	15,126	23/120	37.6

[a] Physiologic factors used to calculate exposure of 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) = $\frac{\text{ADD x Exposure days in a time period or season}}{\text{Days in a time period or season}}$

Results: ADD = 196.4 µg/kg/day; SADD = 13.05 µg/kg/day.

A. Exposure of residents/bystanders to MITC: Adults

Results of ambient air monitoring for MITC from five studies (A.2, A.4, A.7, A.8, and A.9) were used in the estimation of exposure of residents/bystanders. Application rates in study A.4 was 318 lb a.i. per acre and 159.8 for study A.9. The application rates in A.2, A.7 and A.8 were not mentioned in the report because those were ambient MITC monitoring studies; these three studies were not directly associated with metam-sodium applications. Therefore, the exposure estimates were not corrected for the maximum label rate. In order to normalize the exposure estimates, metam-sodium application rates were adjusted to reflect a maximum label rate for soil application of 318 lb a.i. per acre. Studies A.1, A.3, A.5, A.6 were included in the following discussion for historical purposes only.

A.1 Air monitoring in Contra Costa County

Ambient air monitoring for MITC was conducted after a ground 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 (53-55 °F). The application of metam-sodium (32.7%, 3.18 lb a.i./gal) was done by soil injection at a rate of 18 gal/A equivalent to 57 lb a.i./A. 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 sampling tubes (SKC Catalog No. 226-09), containing 400 mg charcoal in the primary and 200 mg in the secondary section, 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: one approximately 15 yards from the northern perimeter and two approximately 15 yards from the southern perimeter of the treated field. Duplicate samples were obtained from all 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 to 1.82 m^3.

Samples were analyzed by a gas chromatograph equipped with a nitrogen/phosphorous detector. Minimum detection limit was 0.075 µg/sample. The recovery levels for the 1 µg/tube spikes ranged from 68 to 72%, averaging 70%. MITC was not detected in three background samples. Short-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 8a (male), 8b (female), and 14 (children). Moderate-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 9a (male), 9b (female), and 15 (children).

A.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. Sampling stations were set up at four sites: Shafter, Bakersfield, Lamont and Weed Patch. Application rates of metam-sodium near the sampling stations were not mentioned in the report. 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 all four sites. 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%. The MDL was 0.03 µg/sample (0.01 $\mu g/m^3$). Short-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 8a (male), 8b (female), and 14 (children). Moderate-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 9a (male), 9b (female), and 15 (children).

A.3 Ambient air monitoring in Kern County during summer 1993 after a ground injection application of metam-sodium to a field

A 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 (A.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 lb a.i. 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 and one was 40 yards from the field perimeter. Sampling equipment and methods were similar to that described in A.1. Average flow rate of air through sampling tubes was 1.88 L/min. Duplicate samples were obtained from all 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. The field spiked recovery of 67% in A.2 (CARB, 1994a) was arbitrarily used to adjust exposure levels because CARB conducted this and the A.2 study. Short-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 8a (male), 8b (female), and 14 (children). Moderate-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 9a (male), 9b (female), and 15 (children).

A.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 °F) at the highest allowable application rate of 100 gallons of metam-sodium (Vapam®) per acre, equivalent to 318 lb a.i. per acre.

Air samples of MITC and carbon disulfide (CS_2) were collected using two-stage (400/200 mg) coconut charcoal vapor-collection tubes (SKC) mounted to personal SKC personal air sampling pumps (Model No. 224PCXR7). SKC (560/260 mg) silica gel tubes 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. 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 absorbed dosages of MITC are shown in Tables 8a (male), 8b (female), and 14 (children). Moderate-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 9a (male), 9b (female), and 15 (children).

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 8a. Short-term air concentrations and absorbed daily dosages of MITC from eight studies: Exposure of adult males.[a]

	Method of application/ sampling site	n[b]	Air conc. (TWA) Mean (Range) (ppb)	ADD Mean (Range) (µg/kg/day)
A.1[c] Contra Costa County (CARB, 1993) (Cool air & cool soil, 53-55 °F)	Soil injection	2	618 (597-646)	514 (497-537)
A.2 Kern County (CARB, 1994a)	Not reported			
(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
A.3[c] Kern County (CARB, 1994b) (Warm air, 61-92 °F) (Warm soil, 79-88 °F)	Soil injection	3	472 (70-827)	392 (58.6-688)
A.4 Kern County (Wofford *et al.*, 1994)	Fixed-set sprinklers			
(Warm air & warm soil, 80-86 °F)	5 meters	5	1102 (61.3-2853)	917 (51.0-2374)
	75 meters	5	878 (2.67-2813)	731 (2.22-2341)
	150 meters	5	468 (2.67-1760)	390 (2.22-1465)
A.5[c] Madera (Zeneca, 1993)	Fixed-set sprinklers			
(Warm soil, 58-88 °F)	5 meters	6	186 (17.0-419)	155 (14.1-349)
(Warm air, 53-94 °F)	25 meters	6	171 (12.8-348)	142 (10.6-290)
	125 meters	6	118 (20.2-273)	98.5 (16.8-227)
	500 meters	6	22.8 (2.93-54.4)	19.0 (2.44-45.3)
A.6[c] Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F)	Soil injection	1	236	196
A.7 Bakersfield (Seiber *et al.*, 1999)	Not reported			
(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	0.08	0.22
A.8 Lompoc (DPR, 1999d)	Not reported	1	0.25	0.21
A.9 Kern County (MSTF, 1999)	Please see pages 26-31			

[a] 1). Mean (arithmetic) air concentrations and ADDs are based on the short-term and downwind (except A.7 and A.8) air monitoring data, e.g., 24-hour-TWA or closest to 24-hour-TWA, except for A.2 and A.6 where air concentration represents the highest, downwind air concentration. The range is not the TWA value.
2). The application rates for A.2, A.7, and A.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 absorbed dosages of MITC from these three studies were not corrected for the maximum application rate of metam-sodium.

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

[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.

Table 8b. Short-term air concentrations and absorbed daily dosages of MITC from eight studies: Exposure of adult females.[a]

	Method of application/ sampling site	n[b]	Air conc. (TWA) Mean (Range) (ppb)	ADD Mean (Range) (µg/kg/day)
A.1[c] Contra Costa County (CARB, 1993) (Cool air & cool soil, 53-55 °F)	Soil injection	2	618 (597-646)	352 (340-368)
A.2 Kern County (CARB, 1994a)	Not reported			
(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
A.3[c] Kern County (CARB, 1994b) (Warm air, 61-92 °F) (Warm soil, 79-88 °F)	Soil injection	3	472 (70-827)	269 (40.1-471)
A.4 Kern County (Wofford *et al.*, 1994)	Fixed-set sprinklers			
(Warm air & warm soil, 80-86 °F)	5 meters	5	1102 (61.3-2853)	628 (35.0-1626)
	75 meters	5	878 (2.67-2813)	500 (1.52-1603)
	150 meters	5	468 (2.67-1760)	267 (1.52-1003)
A.5[c] Madera (Zeneca, 1993)	Fixed-set sprinklers			
(Warm soil, 58-88 °F)	5 meters	6	186 (17.0-419)	106 (9.66-239)
(Warm air, 53-94 °F)	25 meters	6	171 (12.8-348)	97.3 (7.28-198)
	125 meters	6	118 (20.2-273)	67.4 (11.5-156)
	500 meters	6	22.8 (2.93-54.4)	13.1 (1.67-31.0)
A.6[c] Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F)	Soil injection	1	236	135
A.7 Bakersfield (Seiber *et al.*, 1999)	Not reported			
(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	0.08	0.15
A.8 Lompoc (DPR, 1999d)	Not reported	1	0.25	0.14
A.9 Kern County (MSTF, 1999)	Please see pages 26-31			

[a] 1). Mean (arithmetic) air concentrations and ADDs are based on the short-term and downwind (except A.7 and A.8) air monitoring data, e.g., 24-hour-TWA or closest to 24-hour-TWA, except for A.2 and A.6 where air concentration represents the highest, downwind air concentration. The range is not the TWA value.
2). The application rates for A.2, A.7, and A.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 absorbed dosages of MITC from these three studies were not corrected for the maximum application rate of metam-sodium.

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

[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.

Table 9a. Moderate-term air concentrations and seasonal average daily dosages of MITC from eight studies: Exposure of adult males.[a]

	Method of application/ sampling site	n[b]	Air conc. (TWA) Mean (Range) (ppb)	SADD Mean (Range) (µg/kg/day)
A.1[c] Contra Costa County (CARB, 1993) (Cool air & cool soil, 53-55 °F)	Soil injection	7	246 (0.14-646)	39.2 (0.02-103)
A.2 Kern County (CARB, 1994a)	Not reported			
(Warm air & warm soil)	Shafter site	8	0.17 (0.004-1.08)	0.12 (0.003-0.78)
(Temp. range was not given)	Bakersfield site	8	1.01 (0.15-2.92)	0.73 (0.11-2.11)
	Lamont site	8	2.85 (0.20-8.32)	2.05 (0.15-6.00)
	Weed Patch site	8	4.09 (0.93-8.76)	2.95 (0.67-6.32)
A.3[c] Kern County (CARB, 1994b) (Warm air, 61-92 °F) (Warm soil, 79-88 °F)	Soil injection	8	229 (2.36-827)	36.6 (0.38-132)
A.4 Kern County (Wofford *et al.*, 1994)	Fixed-set sprinklers			
(Warm air & warm soil, 80-86 °F)	5 meters	9	419 (3.04-2853)	66.8 (0.48-455)
	75 meters	9	338 (1.33-2813)	54.0 (0.21-449)
	150 meters	6	322 (2.67-1760)	51.3 (0.43-281)
A.5[c] Madera (Zeneca Inc., 1993)	Fixed-set sprinklers			
(Warm soil, 58-88 °F)	5 meters	13	101 (8.83-419)	16.1 (1.41-66.8)
(Warm air, 53-94 °F)	25 meters	13	95.7 (10.3-348)	15.3 (1.64-55.5)
	125 meters	13	63.8 (3.50-273)	10.2 (0.56-43.6)
	500 meters	13	13.1 (1.29-54.4)	2.08 (0.21-8.68)
A.6[c] Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F)	Soil injection	6	81.9 (0.59-236)	13.1 (0.09-37.7)
A.7 Bakersfield (Seiber *et al.*, 1999)	Not reported			
(Summer)	Lamont: houses	43	1.07 (0.05-5.94)	0.77 (0.04-4.28)
	Lamont: environment	14	0.94 (0.10-2.53)	0.68 (0.07-1.82)
	Weedpatch: environ.	12	1.39 (0.10-4.76)	1.0 (0.07-3.43)
	Shafter: houses	45	0.46 (0.03-6.55)	0.33 (0.02-4.7)
	Shafter: environment	15	0.59 (0.02-7.70)	0.43 (0.02-5.55)
(Winter)	Lamont: houses	16	0.37 (0.05-1.21)	0.26 (0.04-0.87)
	Weedpatch: environ.	8	0.50 (0.03-1.63)	0.36 (0.02-1.18)
	Arvin: houses	15	0.18 (0.03-0.74)	0.13 (0.02-0.53)
	Arvin: environ.	6	0.13 (0.03-0.27)	0.10 (0.02-0.19)
A.8 Lompoc (DPR, 1999d)	Not reported	1	0.0007	0.0005
A.9 Kern County (MSTF, 1999)	Please see pages 26-31			

[a] 1). Mean (arithmetic) air concentrations and ADDs are based on the short-term and downwind (except A.7 and A.8) air monitoring data, e.g., sample collection times were 69 hours (A.1), 187 hours (A.2 for Shafter site), 66 hours (A.3), and 73.5 hours (A.4 for 5 meters). The range is not the TWA value.
2). The application rates for A.2, A.7, and A.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 absorbed dosages of MITC from these three studies were not corrected for the maximum application rate of metam-sodium.

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

[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.

Table 9b. Moderate-term air concentrations and seasonal average daily dosages of MITC from eight studies: Exposure of adult females.[a]

	Method of application/ sampling site	n[b]	Air conc. (TWA) Mean (Range) (ppb)	SADD Mean (Range) (µg/kg/day)
A.1[c] Contra Costa County (CARB, 1993) (Cool air & cool soil, 53-55 °F)	Soil injection	7	246 (0.14-646)	26.85 (0.01-70.5)
A.2 Kern County (CARB, 1994a)	Not reported			
(Warm air & warm soil)	Shafter site	8	0.17 (0.004-1.08)	0.08 (0.002-0.53)
(Temp. range was not given)	Bakersfield site	8	1.01 (0.15-2.92)	0.50 (0.07-1.44)
	Lamont site	8	2.85 (0.20-8.32)	1.41 (0.10-4.11)
	Weed Patch site	8	4.09 (0.93-8.76)	2.02 (0.46-4.33)
A.3[c] Kern County (CARB, 1994b) (Warm air, 61-92 °F) (Warm soil, 79-88 °F)	Soil injection	8	229 (2.36-827)	25.0 (0.26-90.3)
A.4 Kern County (Wofford *et al.*, 1994)	Fixed-set sprinklers			
(Warm air & warm soil, 80-86 °F)	5 meters	9	419 (3.04-2853)	45.7 (0.33-312)
	75 meters	9	338 (1.33-2813)	36.94 (0.15-307)
	150 meters	6	322 (2.67-1760)	35.14 (0.29-192)
A.5[c] Madera (Zeneca 1993)	Fixed-set sprinklers			
(Warm soil, 58-88 °F)	5 meters	13	101 (8.83-419)	11.0 (0.96-45.8)
(Warm air, 53-94 °F)	25 meters	13	95.7 (10.3-348)	10.5 (1.13-38.0)
	125 meters	13	63.8 (3.50-273)	6.96 (0.38-29.8)
	500 meters	13	13.1 (1.29-54.4)	1.43 (0.14-5.95)
A.6[c] Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F)	Soil injection	6	81.9 (0.59-236)	8.94 (0.06-25.8)
A.7 Bakersfield (Seiber *et al.*, 1999)	Not reported			
(Summer)	Lamont: houses	43	1.07 (0.05-5.94)	0.53 (0.03-2.93)
	Lamont: environment	14	0.94 (0.10-2.53)	0.47 (0.05-1.25)
	Weedpatch: environ.	12	1.39 (0.10-4.76)	0.69 (0.05-2.35)
	Shafter: houses	45	0.46 (0.03-6.55)	0.23 (0.01-3.24)
	Shafter: environment	15	0.59 (0.02-7.70)	0.29 (0.01-3.80)
(Winter)	Lamont: houses	16	0.37 (0.05-1.21)	0.18 (0.03-0.60)
	Weedpatch: environ.	8	0.50 (0.03-1.63)	0.25 (0.01-0.81)
	Arvin: houses	15	0.18 (0.03-0.74)	0.09 (0.01-0.37)
	Arvin: environ.	6	0.13 (0.03-0.27)	0.07 (0.01-0.13)
A.8 Lompoc (DPR, 1999d)	Not reported	1	0.0007	0.0003
A.9 Kern County (MSTF, 1999)	Please see pages 26-31			

[a] 1). Mean (arithmetic) air concentrations and ADDs are based on the short-term and downwind (except A.7 and A.8) air monitoring data, e.g., sample collection times were 69 hours (A.1), 187 hours (A.2 for Shafter site), 66 hours (A.3), and 73.5 hours (A.4 for 5 meters). The range is not the TWA value.
2). The application rates for A.2, A.7, and A.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 absorbed dosages of MITC from these three studies were not corrected for the maximum application rate of metam-sodium.

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

[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.

A.5 Exposure estimates for residents and bystanders to MITC

This study was conducted to monitor off-site movement of MITC during and after an application of metam-sodium (Zeneca Inc., 1993). 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 by using fixed-set sprinklers. The test site was cultivated and disked. 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 lb a.i. per acre. The soil temperatures during the study (three inches into the soil) ranged from 58 to 88 °F and the air temperatures ranged from 53 to 94 °F.

Ambient air concentrations of MITC were monitored in four distances 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 high volume 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. Downwind sampling stations were established perpendicular to the prevailing northwest wind direction at 5, 25, 125, and 500 meters from the downwind edge of the application swath. 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.

For the exposure estimation of residents and bystanders, average concentration of MITC at each distance collected for 24 hours was used. Short-term air concentrations and estimated absorbed

dosages of MITC are shown in Tables 8a (male), 8b (female), and 14 (children). Moderate-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 9a (male), 9b (female), and 15 (children).

A.6 Air monitoring in Kern County in August 1995

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 °F and that for ambient air ranged from 59.7 to 98.8 °F. The wind speed ranged from 1.4 to 8.0 miles per hour. The application of metam-sodium (33%, 3.1 lb a.i./gal) was done by soil injection at a rate of 50 gal/A equivalent to 155 lb a.i./A. 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 sampling tubes (SKC Catalog No. 226-09), containing 400 mg charcoal in the primary and 200 mg in the secondary section, 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 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%. MITC was detected in the background samples. However, the MITC results were not corrected for the low background levels, which ranged from 0.08 to 0.18 ppb. Short-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 8a (male), 8b (female), and 14 (children). Moderate-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 9a (male), 9b (female), and 15 (children).

Methyl isocyanate (MIC) in XAD-7 tubes collected from this study was also analyzed. Samples were desorbed with acetonitrile and analyzed by high performance liquid chromatography using a fluorescence detector. The limit of detection in terms of air concentrations is 74 ng/m^3 or 0.032 ppbv. The limit of quantitation in terms of air concentration is 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.

A.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 °C 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 air flow 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 limit of quantitation (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) will be 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 and SADD 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/bystanders would be exposed to MITC available in the AM and PM periods, and indoor and/or outdoor sites. ADD was estimated from highest daily MITC air concentration of each sampling station;

SADD was estimated from the average of daily MITC concentrations of each sampling station during summer or winter. Short-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 8a (male), 8b (female), and 14 (children). Moderate-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 9a (male), 9b (female), and 15 (children).

A.8 Air monitoring study in Lompoc.

Ambient air concentrations of MITC and other pesticides in Lompoc (DPR, 1999d) 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 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 ug/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 air concentration was 0.002 ug/m^3. Short-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 8a (male), 8b (female), and 14 (children). Moderate-term air concentrations and estimated absorbed dosages of MITC are shown in Tables 9a (male), 9b (female), and 15 (children).

A.9 Off-site air movement from the application of metam-sodium through shank injection and sprinkler irrigation in Kern County in 1999.

In June 1999, Agrisearch Incorporated conducted a study sponsored by the MSTF to determine methyl isothiocyanate off-site air movement from the application of metam-sodium through shank injection and sprinkler irrigation (MSTF, 1999). 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 (Vapam® HL, 4.26 lb a.i./gallon) per treated acre to a 79-acre carrot field. This application rate was 37.5 gallons (equivalent to 159.8 lb a.i.) 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 California Technical Information Bulletin (TIB) "Guidelines for Metam-Sodium Application Methods in California" (February 1999). The purpose of the TIB is to minimize off-site movement of odors when applying metam-sodium.

For sprinkler irrigation, the odor control measures required by the product label and TIB included: pre-application irrigation, applied when air temperature <90 °F, applied when wind speed was ≤7 mph, applied when there was no thermal inversion near or at the ground, ½ inch water cap immediately post application, and an additional ½ inch water cap within 24 hours post

application. For shank injection, the odor control measures included pre-application irrigation, applied when soil temperature <90 °F, soil cap at application, and ½ inch water cap immediately post application.

The charcoal sorbent tube (400/200 mg charcoal) (SKC 226-09) was used to collect MITC in air. The tube was 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 liter/min. Each tube was used to collect air sample for four hours.

Before the study initiation, a limit of quantitation (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. The method try out data suggested 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 were changed during the study periods. 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%).

Tables 10 and 11 show short- and moderate-term MITC air concentrations at various distances from the treated fields. These air concentrations were not corrected for fortification recoveries because overall recoveries were deemed appropriate. Air concentrations obtained from the study using shank injection were adjusted to reflect a label rate of 75 gallons of formulation per treated 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 moderate-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. See footnotes of Table 10 for further explanation.

Exposure of residents was calculated for adult males, adult females and children. Off-site MITC air concentrations obtained from the study are not the same as a typical ambient air monitoring study where sampling stations are not set near treated fields. Therefore, 23 exposure days in a 120-day period will be used to calculate moderate-term exposure. Short- and moderate-term term air concentrations and estimated absorbed dosages of MITC are shown in Tables 12 (males) and 13 (females).

Table 10. Off-site MITC air concentrations after the application of metam-sodium using sprinkler irrigation.

Distance (m)	Sampling station	Short-term (TWA[a], ppb) (for ADD) Day 1[b]	Day 2[b]	Day 3[b]	Day 4[b]	Moderate-term (ppb) (for SADD) 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] TWA (time-weighted average) = $(C_1T_1 + C_2T_2 + \ldots\ldots C_nT_n)/(T_1 + T_2 + \ldots\ldots T_n)$. C_1 is MITC concentration at time T_1, C_n is MITC concentration at time T_n.

[b] example, 101 ppb for day 1 is the time-weighted average (TWA) of 6 MITC air concentrations collected at the sampling station A for about 24 hours. The distance of this sampling station was 150 m from the treated field.

[c] example, 63 ppb for days 1-4 is an average of daily MITC air concentrations from the sampling station A. The distance of this sampling station was 150 m from the treated field.

[d] example, 55 ppb is an average of MITC air concentrations from moderate-term air concentrations of stations A, B, and D. The distance of the se sampling stations was 150 m from the treated field.

Table 11. Off-site MITC air concentrations after the application of metam-sodium using shank injection.

Distance (m)	Sampling station	Short-term (TWA[a], ppb) (for ADD) Day 1[b]	Day 2[b]	Day 3[b]	Day 4[b]	Moderate-term (ppb) (for SADD) 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	39	
	B	32	47	24	6.7	28	29
	C	24	32	17	6	20	
837 (upwind)	A	78	18	28	4.7	33	
	B	106	62	28	4	51	

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

[b] example, 140 ppb for day 1 is the time-weighted average (TWA) of 6 MITC air concentrations collected at the sampling station A for about 24 hours. The distance of this sampling station was 150 m from the treated field.

[c] example, 94 ppb for days 1-4 is an average of daily MITC air concentrations from the sampling station A. The distance of this sampling station was 150 m from the treated field.

[d] example, 67 ppb is an average of MITC air concentrations from moderate-term air concentrations of stations A, B, and D. The distance of the se sampling stations was 150 m from the treated field.

Table 12. Exposure of male residents to off-site MITC generated from the application of metam-sodium.

1. Sprinkler irrigation

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

2. Shank injection

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

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

[b] ADD (absorbed daily dosage, μg/kg body weight/day) = [$\mu g/m^3$ (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) = (ADD x Exposure days in a time period or season)/Days in a time period or season

Table 13. Exposure of female residents to off-site MITC generated from the application of metam-sodium.

1. Sprinkler irrigation

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

2. Shank injection

Distance (m)	Short-term exposure: Sampling station		MITC (TWA)[a] (ppb)	ADD[b] (µg/kg/day)	Moderate-term exposure: Sampling station	MITC (TWA)[a] Days 1-4		SADD[c] (µg/kg/day)
150	D	Low	5.4	3.05	B	Low	51	5.51
	A	High	175	99.2	A	High	94	10.3
						Mean	67	7.33
300	C	Low	5.4	3.05	C	Low	29	3.14
	A	High	106	60.1	A	High	56	6.09
						Mean	39	4.23
486	C	Low	6	3.43	C	Low	20	2.19
	A	High	84	47.8	A	High	39	4.23
						Mean	29	3.14
837	B	Low	4	2.28	A	Low	33	3.54
(upwind)	B	High	106	60.5	B	High	51	5.51

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

[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) = (ADD x Exposure days in a time period or season)/Days in a time period or season

B. Exposure of children to MITC

Children can be exposed to airborne MITC from nearby fumigated fields similar to adults as described above. 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 absorbed dosages of MITC are shown in Table 14. Moderate-term air concentrations and estimated absorbed dosages of MITC are shown in Table 15. Exposures of children to short- and moderate-term air concentrations obtained from a study sponsored by the MSTF (1999) were also estimated and are shown in Table 16.

Table 14. Short-term air concentrations and absorbed daily dosages of MITC from eight studies: Exposure of children.[a]

	Method of application/ sampling site	n[b]	Air conc. (TWA) Mean (Range) (ppb)	ADD Mean (Range) (µg/kg/day)
A.1[c] Contra Costa County (CARB, 1993) (Cool air & cool soil, 53-55 °F)	Soil injection	1	618 (597-646)	1388 (1342-1450)
A.2 Kern County (CARB, 1994a)	Not reported			
(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
A.3[c] Kern County (CARB, 1994b) (Warm air, 61-92 °F) (Warm soil, 79-88 °F)	Soil injection	3	472 (70-827)	1058 (158-1858)
A.4 Kern County (Wofford *et al.*, 1994)	Fixed-set sprinklers			
(Warm air & warm soil, 80-86 °F)	5 meters	5	1102 (61.3-2853)	2476 (138-6410)
	75 meters	5	878 (2.67-2813)	1974 (6.00-6321)
	150 meters	5	468 (2.67-1760)	1053 (6.00-3956)
A.5[c] Madera (Zeneca Inc., 1993)	Fixed-set sprinklers			
(Warm soil, 58-88 °F)	5 meters	6	186 (17-419)	418 (38.1-942)
(Warm air, 53-94 °F)	25 meters	6	171 (12.8-348)	383 (28.6-783)
	125 meters	6	118 (20.2-273)	266 (45.4-613)
	500 meters	6	22.8 (2.93-54.4)	51.3 (6.59-122)
A.6[c] Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F)	Soil injection	1	236	529
A.7 Bakersfield (Seiber *et al.*, 1999)	Not reported			
(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	0.08	0.59
A.8 Lompoc (DPR, 1999d)	Not reported	1	0.25	0.57
A.9 Kern County (MSTF, 1999)	Please see pages 26-29 and 37			

[a] 1). Mean (arithmetic) air concentrations and ADDs are based on the short-term and downwind (except A.7 and A.8) air monitoring data, e.g., 24-hour-TWA or closest to 24-hour-TWA, except for A.2 and A.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 A.2, A.7, and A.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 absorbed dosages of MITC from these studies were not corrected for the maximum application rate of metam-sodium.

3). The absorbed doses for male children are assumed to be similar to those for female children.

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

[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.

Table 15. Moderate-term air concentrations and seasonal average daily dosages of MITC from eight studies: Exposure of children.[a]

	Method of application/ sampling site	n[b]	Air conc. (TWA) Mean (Range) (ppb)	SADD Mean (Range) (µg/kg/day)
A.1[c] Contra Costa County (CARB, 1993) (Cool air & cool soil, 53-55 °F)	Soil injection	7	246 (0.14-646)	106 (0.05-278)
A.2 Kern County (CARB, 1994a)	Not reported			
(Warm air & warm soil)	Shafter site	8	0.17 (0.004-1.08)	0.32 (0.008-2.11)
(Temp. range was not given)	Bakersfield site	8	1.01 (0.15-2.92)	1.97 (0.30-5.70)
	Lamont site	8	2.85 (0.20-8.32)	5.54 (0.41-16.2)
	Weed Patch site	8	4.09 (0.93-8.76)	8.0 (1.81-17.0)
A.3[c] Kern County (CARB, 1994b) (Warm air, 61-92 °F) (warm soil, 79-88 °F)	Soil injection	8	229 (2.36-827)	98.8 (1.03-356)
A.4 Kern County (Wofford *et al.*, 1994)	Fixed-set sprinklers			
(Warm air & warm soil, 80-86 °F)	5 meters	9	419 (3.04-2853)	180 (1.30-1229)
	75 meters	9	338 (1.33-2813)	146 (0.57-1212)
	150 meters	6	322 (2.67-1760)	139 (1.16-759)
A.5[c] Madera (Zeneca Inc., 1993)	Fixed-set sprinklers			
(Warm soil, 58-88 °F)	5 meters	13	101 (8.83-419)	43.4 (3.81-180)
(warm air, 53-94 °F)	25 meters	13	95.7 (10.3-348)	41.3 (4.43-150)
	125 meters	13	63.8 (3.50-273)	27.5 (1.51-118)
	500 meters	13	13.1 (1.29-54.4)	5.62 (0.57-23.4)
A.6[c] Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F)	Soil injection	6	81.9 (0.59-236)	35.4 (0.24-102)
A.7 Bakersfield (Seiber *et al.*, 1999)	Not reported			
(Summer)	Lamont: houses	43	1.07 (0.05-5.94)	2.10 (0.11-11.56)
	Lamont: environment	14	0.94 (0.10-2.53)	1.84 (0.19-4.91)
	Weedpatch: environ.	12	1.39 (0.10-4.76)	2.7 (0.19-9.26)
	Shafter: houses	45	0.46 (0.03-6.55)	0.89 (0.05-12.8)
	Shafter: environment	15	0.59 (0.02-7.70)	1.16 (0.05-15.0)
(Winter)	Lamont: houses	16	0.37 (0.05-1.21)	0.70 (0.11-2.35)
	Weedpatch: environ.	8	0.50 (0.03-1.63)	0.97 (0.05-3.19)
	Arvin: houses	15	0.18 (0.03-0.74)	0.35 (0.05-1.43)
	Arvin: environ.	6	0.13 (0.03-0.27)	0.27 (0.05-0.51)
A.8 Lompoc (DPR, 1999d)	Not reported	1	0.0007	0.001
A.9 Kern County (MSTF, 1999)	Please see pages 26-29 and 37			

[a] 1). Mean (arithmetic) air concentrations and SADDs are based on the moderate-term and downwind (except A.7 and A.8) air monitoring data, e.g., sample collection times were 53 hours (A.1), 240 hours (A.2), 64 hours (A.3), and 74 hours (A.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 A.2, A.7, and A.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 absorbed dosages of MITC were not corrected for the maximum application rate of metam-sodium.

3). The absorbed dosages for male children are assumed to be similar to those for female children.

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

[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.

Table 16. Exposure of children to off-site MITC generated from the application of metam-sodium.

1. Sprinkler irrigation

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

2. Shank injection

Distance (m)	Short-term exposure: Sampling station		MITC (TWA)[a] (ppb)	ADD[b] (µg/kg/day)	Moderate-term exposure: Sampling station	MITC (TWA)[a] Days 1-4		SADD[c] (µg/kg/day)
150	D	Low	5.4	12.2	B	Low	51	22.02
	A	High	175	396	A	High	94	40.98
						Mean	67	29.31
300	C	Low	5.4	12.2	C	Low	29	12.54
	A	High	106	240	A	High	56	24.36
						Mean	39	16.92
486	C	Low	6	13.7	C	Low	20	8.75
	A	High	84	191	A	High	39	16.92
						Mean	29	12.54
837 (upwind)	B	Low	4	9.13	A	Low	33	14.15
	B	High	106	242	B	High	51	22.02

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

[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) = (ADD x Exposure days in a time period or season)/Days in a time period or season

C. The use of metam-sodium for treating sewer systems

In 2002, three metam-sodium containing products, Sanafoam® Vaporooter II®, Sewerout™, and Sewerout II™ are used to destroy infiltrating roots in sewer systems (DPR, 2002).

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. Overexposure 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.

D. Short-term MITC air concentrations: Summary

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 (A.1-A.9). Previously, MITC concentrations were calculated as 24- or closest to 24-hour TWA values for short-term exposures. 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 NOEL values for MITC relate directly only to 1, 4 or 8-hour exposures.

The sampling periods used in the above mentioned studies varied tremendously. In order to estimate 1- and 8-hour MITC air concentrations (Table 17), the following assumptions are used whenever they are applicable.

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, e.g., 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.	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.

Table 17. 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
A.1[c] Contra Costa County (CARB, 1993) (Cool air & cool soil, 53-55 °F)	Soil injection	646	646	625-min. sampling time
A.2 Kern County (CARB, 1994a)	Not reported			
(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
A.3[c] Kern County (CARB, 1994b) (Warm air, 61-92 °F) (Warm soil, 79-88 °F)	Soil injection	827	827	785-min. sampling time
A.4 Kern County (Wofford *et al.*, 1994)	Fixed-set sprinklers			
(Warm air & warm soil, 80-86 °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
A.5[c] Madera (Zeneca, 1993)	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
A.6[c] Bakersfield (CARB, 1997) (Soil 78-86 °F, air 59.7-98.8 °F)	Soil injection	236	236	760-min. sampling time
A.7 Bakersfield (Seiber *et al.*, 1999)	Not reported			
(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
A.8 Lompoc (DPR, 1999d)	Not reported	0.3	0.3	Shown as the 24-hour TWA

Table 17 (continued).

Location	Method of application/ sampling station	Air concentrations of MITC (ppb)[e] 1-hour[a]	8-hour[f]
A.9 Bakersfield (MSTF, 1999)	Sprinkler irrigation		
	A 150 meters	234	195
	A 300 meters	148	133
	A 700 meters	99	90
	A 970 meters	15	8.3
	B 150 meters	275	191
	B 300 meters	200	124
	B 700 meters	63	53
	B 970 meters	41	32
	C 300 meters	194	133
	C 700 meters	50	31
	D 150 meters	281	193
	Shank injection		
	A 150 meters	281	244
	A 300 meters	216	151
	A 486 meters	199	123
	A 837 meters	43	38
	B 150 meters	131	88
	B 300 meters	101	74
	B 486 meters	109	67
	B 837 meters	242	149
	C 300 meters	67	59
	C 486 meters	39	33
	D 150 meters	144	141

[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] Values may not represent downwind MITC because the wind directions changed during the study.
[f] Approximately the 8-hour TWA of two consecutive samples.

EXPOSURE APPRAISAL

Air concentrations of MITC and the estimated dosages for short- and moderate-term exposures were obtained from field studies. This document emphasizes the exposures of persons to MITC generated from metam-sodium used in agriculture. Even though dazomet can produce MITC, the amount is insignificant compared to that generated from metam-sodium.

Defaults for 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, number of workdays or exposure days per time period or season were estimated from available information. A large scale survey for these time periods is not feasible at this time.

Silica gel drying tubes were used in two of the studies for application site and ambient air monitoring studies (Zeneca Inc., 1993; Wofford *et al.*, 1994). MITC in this portion of the sampling train was not analyzed, except for 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 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. Air concentrations obtained from the study conducted by Wofford *et al.* (1994) were significantly higher than those from Zeneca Inc. (1993). 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 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 field exposure study sponsored by the MSTF (1999) is similar to the study conducted by Zeneca Inc. (1993). However, results indicated that some MITC air concentrations obtained from the MSTF study may not represent downwind air concentrations. Four exposure studies (CARB, 1993, CARB, 1994b, Zeneca, 1993, and CARB, 1997) were included in this report to provide historical perspective only because the studies were not conducted in compliance with the current TIB.

There is convincing evidence that extrapolation of exposure from a short monitoring period would contribute to overestimation of exposure. A study by Spencer *et al.* (1995) showed that if a full day's exposure was extrapolated from a 1/3 workday monitoring period, the exposure would be overestimated by 50-80% and from a 1/2 workday, 20-40%. The results from this study may be applicable to the field monitoring study MITC, especially for handlers. Sample collection times for metam-sodium applicators ranged from 15 to 120 minutes. Extrapolation of exposure from a short monitoring period to a full workday or 8 hours would likely overestimate exposure by 50-80%. However, short-term (e.g., 1- or 4-hour) MITC concentrations may be under estimated 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. Furthermore, the degree of underestimation is not known.

It is important to note that the applications of metam-sodium in some of those studies were not done in accordance with the current TIB. Samples of some air monitoring studies were collected within the buffer zones. The exposure estimates from these studies may overestimate the actual exposure for workers and residents/bystanders. MITC concentrations in air obtained from the

study sponsored by the MSTF are likely underestimated because evidence indicated that not all sampling stations were located in the downwind direction.

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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