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# Dazomet Soil Incorporation:
## WorksheetMaker Workbook Documentation
## Final Report

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# ACRONYMS, ABBREVIATIONS, AND SYMBOLS

| | |
|---|---|
| ACGIH | American Conference of Governmental Industrial Hygienists |
| ADI | Acceptable Daily Intake |
| AEL | adverse-effect level |
| a.e. | acid equivalent |
| a.i. | active ingredient |
| a.k.a. | also known as |
| a.s. | active substance |
| AOEL | acceptable occupational exposure limit |
| APHIS | Animal and Plant Health Inspection Service |
| ATSDR | Agency for Toxic Substances and Disease Registry |
| ASAE | American Society of Agricultural Engineers |
| BCF | bioconcentration factor |
| bw | body weight |
| calc | calculated value |
| CBI | confidential business information |
| CI | confidence interval |
| cm | centimeter |
| CNS | central nervous system |
| COC | crop oil concentrates |
| DAA | days after application |
| DAT | days after treatment |
| DER | data evaluation record |
| d.f. | degrees of freedom |
| EC | emulsifiable concentrate |
| $EC_x$ | concentration causing X% inhibition of a process |
| $EC_{25}$ | concentration causing 25% inhibition of a process |
| $EC_{50}$ | concentration causing 50% inhibition of a process |
| ECOTOX | ECOTOXicology (database used by U.S. EPA/OPP) |
| EFED | Environmental Fate and Effects Division (U.S. EPA/OPP) |
| ERA | ecological risk assessment |
| ExToxNet | Extension Toxicology Network |
| F | female |
| FH | Forest Health |
| FIFRA | Federal Insecticide, Fungicide and Rodenticide Act |
| FQPA | Food Quality Protection Act |
| g | gram |
| GLP | Good Laboratory Practices |
| ha | hectare |
| HED | Health Effects Division (U.S. EPA/OPP) |
| HHRA | human health risk assessment |
| HIARC | Hazard Identification and Assessment Review Committee (part of U.S. EPA/OPP/HED) |
| HQ | hazard quotient |
| HRAC | Herbicide Resistance Action Committee |
| IARC | International Agency for Research on Cancer |
| IRED | Interim Reregistration Eligibility Decision |

| | |
|---|---|
| IRIS | Integrated Risk Information System |
| $k_a$ | absorption coefficient |
| $k_e$ | elimination coefficient |
| kg | kilogram |
| $K_{o/c}$ | organic carbon partition coefficient |
| $K_{o/w}$ | octanol-water partition coefficient |
| $K_p$ | skin permeability coefficient |
| L | liter |
| lb | pound |
| $LC_{50}$ | lethal concentration, 50% kill |
| $LD_{50}$ | lethal dose, 50% kill |
| LOAEL | lowest-observed-adverse-effect level |
| LOC | level of concern |
| $LR_{50}$ | 50% lethal response [EFSA/European term] |
| m | meter |
| M | male |
| mg | milligram |
| mg/kg/day | milligrams of agent per kilogram of body weight per day |
| mL | milliliter |
| mM | millimole |
| mPa | millipascal, (0.001 Pa) |
| MITC | methyl isothiocyanate |
| MOS | margin of safety |
| MRID | Master Record Identification Number |
| MSDS | material safety data sheet |
| MSO | methylated seed oil |
| MW | molecular weight |
| NOAEL | no-observed-adverse-effect level |
| NOEC | no-observed-effect concentration |
| NOEL | no-observed-effect level |
| NOS | not otherwise specified |
| N.R. | not reported |
| OPP | Office of Pesticide Programs |
| ppm | parts per million |
| RED | re-registration eligibility decision |
| RfD | reference dose |
| SERA | Syracuse Environmental Research Associates |
| T.G.I.A. | Technical grade active ingredient |
| UF | uncertainty factor |
| U.S. | United States |
| USDA | U.S. Department of Agriculture |
| U.S. EPA | U.S. Environmental Protection Agency |
| USGS | U.S. Geological Survey |
| WHO | World Health Organization |

# 1. INTRODUCTION

## 1.1. General Information

This document supports the development of a WorksheetMaker EXCEL workbook for the subject pesticides. As detailed in SERA (2011a), WorksheetMaker is a utility that automates the generation of EXCEL workbooks that accompany Forest Service risk assessments, and these EXCEL workbooks are typically generated in the development of Forest Service risk assessments (SERA 2014).

The development of full Forest Service risk assessments, however, is resource intensive. For some pesticides that are used in only relatively small amounts and/or only in few locations, the development of full Forest Service risk assessments is not feasible. Nonetheless, the Forest Service may be required to develop risk analyses supported by WorksheetMaker EXCEL workbooks. To meet this need, an MS Word utility was developed to facilitate the addition of pesticides and pesticide formulations into the Microsoft Access database used by WorksheetMaker (SERA 2011b). With this addition, WorksheetMaker can be used to generate EXCEL workbooks typical of those that accompany Forest Service risk assessments.

The current document is designed to serve as documentation for the application of this general method for the pesticide discussed in Section 1.2. The major difference between this approach to using WorksheetMaker and the typical use of WorksheetMaker in the development of Forest Service risk assessments involves the level of documentation and the sources used in developing the documentation. While standard Forest Service risk assessments involve a relatively detailed review and evaluation of the open literature and publically available documents from the U.S. EPA, as discussed further in Section 1.2, the current assessment relies primarily on secondary sources with minimal independent evaluation of the data.

## 1.2. Chemical Specific Information

The current document concerns dazomet. Most of the information on dazomet was identified at the U.S. EPA's Pesticide Chemical Search website (http://iaspub.epa.gov/apex/pesticides/f?p=CHEMICALSEARCH:1:5025550978400::NO:1::) using the search term "Dazomet". Files cited in the current document were obtained from the *Regulatory Actions* and *Science Reviews* tabs on this web site. Dazomet is not included in the U.S. EPA's Agency-wide IRIS (Integrated Risk Information System) database (http://www.epa.gov/IRIS/).

Dazomet is a non-selective soil fumigant which can be used to kill fungi, vegetation, and soil nematodes. As a soil fumigant, dazomet is somewhat atypical in that it is applied to soil as a dry granular formulation then incorporated into soil. The current version of WorksheetMaker does not accommodate soil fumigants and does not encompass inhalation exposures (SERA 2011a). Consequently, rather than adding dazomet to the database for WorksheetMaker, this document supports a highly customized EXCEL workbook that is consistent with the conventions used in WorksheetMaker.

Also because soil fumigants are not explicitly covered in the methods document for preparing Forest Service risk assessments (SERA 2014), the current document is somewhat more elaborate than a simple documentation for WorksheetMaker inputs values.

# 2. CHEMICAL/PHYSICAL PROPERTIES

Dazomet was initially registered in the United States in 1967 and was reregistered in 2008 with an amended registration in 2009 (U.S. EPA/OPP 2008a,b, 2009). The U.S. EPA registration review program operates on a 15-year cycle. Dazomet is currently under registration review and the EPA has identified several data needs for dazomet (U.S. EPA/OPP 2014). The data needs are also discussed in the most recent EPA risk assessment of dazomet (U.S. EPA/OPP/EFED 2008, pp. 7-9). The registration review for dazomet is not scheduled for completion until 2019 (U.S. EPA/OPP 2014). Thus, the registration review process will not contribute to the current summary of information on dazomet.

The Forest Service has specified the use of a single formulation, Basamid, presumably referring to Basamid G. The Forest Service has also indicated that the application rate would be 350 lbs/acre (presumably as the formulation) and that up to 40 acres could be treated for a total annual use of 14,000 lbs formulation. Applications would be made in September. Since Basamid G consists of 99% dazomet (AMVAC Chemical Corporation 2011; Certis USA ND), the distinction between application rates in units of formulation versus a.i. is incidental.

Based on an April 29, 2014 posting from AMCAC Chemical Corporation, Basamid G is exclusively distributed by AMVAC Chemical Corporation, a subsidiary of American Vanguard Corporation (http://www.amvac-chemical.com/News-Media/Press-Releases/2014-Press-Releases/April-29-2014-Press-Release). The product label (undated) at the AMVAC website, however, indicates CERTIS USA as the distributer. The most recent product label (December 27, 2011) at the EPA label website (http://iaspub.epa.gov/apex/pesticides/f?p=PPLS:1) lists AMVAC as the manufacturer (U.S. EPA/OPP 2011). The transfer information at the EPA label website (http://iaspub.epa.gov/apex/pesticides/f?p=PPLS:8:17199968499318::NO::P8_PUID:19059) indicates that registration for Basamid G was transferred to BASF on February 20, 2004 and then transferred to CERTIS on December 21, 2010. The current registrant is listed as AMVAC Chemical Corporation. The earliest label at the EPA website (April 11, 1991) identifies BASF as the original registrant. Kegley et al. (2014) indicate that many additional formulations of dazomet are available (i.e., 616 active formulations in the United States). Nevertheless, U.S. EPA/OPP/EFED (2008a, p. 23) indicates that only 20 end-use formulations of dazomet are currently registered.

Table 1 summarizes the chemical and physical properties of dazomet. In terms of potential risks in the use of dazomet, the dominant factor is the rapid conversion of dazomet to methyl isothiocyanate. As discussed in the most recent EPA risk assessment on dazomet (U.S. EPA/OPP/EFED 2008a) and summarized in Table 1, dazomet is rapidly converted to methyl isothiocyanate primarily by hydrolysis—i.e., hydrolysis half-lives of 3 to 9 hours in water and a soil hydrolysis half-time of 17.2 hours. As discussed further in Section 3.2.1.1, soil incorporation of dazomet must be followed by irrigation to facilitate the hydrolysis of dazomet to methyl isothiocyanate. Methyl isothiocyanate forms a vapor which serves as the active soil fumigant. Methyl isothiocyanate is much more persistent than dazomet—e.g., the dissipation half-lives are about 1.5 to 2 days for dazomet and about 10 days for methyl isothiocyanate. In addition, as discussed further in Section 3, methyl isothiocyanate is more toxic than dazomet.

Consequently, methyl isothiocyanate is the agent of concern for most exposure scenarios following applications of dazomet.

# 3. HUMAN HEALTH

## 3.1. Hazard Identification

While full Forest Service risk assessments provide a detailed discussion of the available toxicity data on the pesticide under consideration, this approach is not taken in the current document, in the interest of economy. A reasonably complete discussion of the toxicity data on dazomet and methyl isothiocyanate is provided in U.S. EPA/OPP/HED (2009a). As discussed in U.S. EPA/OPP/HED (2009a, p. 13), the toxicity database on dazomet is reasonably complete; however, the same is not true for methyl isothiocyanate, the major breakdown product of dazomet. Furthermore, the mode of action of methyl isothiocyanate is not well characterized. Additional details of the data needs for dazomet and methyl isothiocyanate are discussed in the EPA's final work plan for the registration review of dazomet (U.S. EPA/OPP 2014).

## 3.2. Exposure Assessment

### 3.2.1. Workers

#### *3.2.1.1. Applications (Dazomet)*

Dazomet, formulated as Basamid G, is applied by soil incorporation, as specified on the product label. A description of the methods used to apply Basamid G at the Forest Service JH Stone Nursery was provided by John Justin (Forest Service Nursery Manager):

> *Currently we are fumigating about 30 acres annually with Dazomet. If our business grows like I hope this could increase to 40 acres annually. The annual acreage would decrease by as much as 10 acres annually if we add some additional herbicides for use in our grass crops through this NEPA effort. We can fumigate a maximum of ten acres per 8 hour day.*
>
> *Fumigation is a complicated process involving at least five staff members. One person is applying the Dazomet with a drop spreader. A second staff member immediately follows behind tilling the fumigant into the soil. A third staff member follows immediately behind the tiller with a roller that compacts the soil to seal the fumigant into the soil. Two or more staff members are irrigating the fields as soon as the other work is done. The fumigated acres are irrigated multiple times a day for at least five days after the chemical application. After five days the fields are dried and then tilled again to release any remaining fumigant gas. All these steps are outline in detail on the label and we follow the label exactly.*
>
> *Last year it took us a week to do 30 acres. All staff are wearing the full PPE required by the label during all work activities and entries into the fields. We also have the equipment to monitor fumigant gas levels in the air. This monitoring allows us to determine safety levels for our staff. All fumigated areas,*

*including the appropriate buffer zones, are closed to all access except trained handlers until the fields are tilled to release the fumigant.*

Based on the above input and as detailed in Worksheet A01 of the EXCEL workbook that accompanies the current document, the exposure assessment is based on a treatment rate of 10 acres per day, an application rate of 350 lbs/acre (Section 1.2), and a field size of 40 acres. These three inputs can be modified in Worksheet A01. As with WorksheetMaker workbooks, changes made in Worksheet A01 are then applied to all calculations in the workbook.

The occupation exposure rates for pesticides typically used in Forest Service risk assessments (SERA 2013) do not include rates for soil incorporation of a granular formulation such as Basamid G. As an alternative, the current assessment adopts the exposure assessment from U.S. EPA/OPP/HED (2009a, pp. 75-76). This exposure assessment is based on exposure rates for granular a formulation from the Pesticide Handlers Exposure Databased (PHED). As detailed in SERA (2014, Section 3.2.2), PHED is a deposition based method for estimating occupational exposures based on exposure rates in units of mg agent per lb a.i. handled. Somewhat atypically, the EPA exposure assessment (U.S. EPA/OPP/HED 2009a) does not explicitly provide exposure rates in terms of mg agent per lb a.i. handled. Instead, the EPA analysis presents Margins of Exposure (MOE) associated with applications at different application rates and field sizes. By definition, the MOE is the exposure divided by a NOAEL. Thus, the underlying exposure rate (***ER*** in units of mg/kg bw per lb handled) can be estimated as:

$$ER_{mg/kg\ per\ lb\ handled} = \frac{NOAEL_{mg/kg\ bw}}{MOE} \div Amt_{lb\ handled} \qquad (1)$$

where ***Tox*** is the toxicity value in units of mg/kg bw, ***MOE*** is the margin of exposure, and ***Amt*** is the amount handled by the worker expressed in units of pounds.

The above method is implemented in Worksheet C01. For calculating the exposure rate, the toxicity value is taken as 1.5 mg/kg bw, which is the animal NOAEL used for occupational exposures to dazomet, as discussed in Section 3.3.17. The EPA analysis gives sets of four MOE baseline exposures: no PPE, gloves, gloves and double layer clothing, and engineering controls. While not explicitly noted in U.S. EPA/OPP/HED (2009a), the term *engineering controls* appears to refer to NIOSH certified full facepiece air-purifying respirators which are required on the product label (Certis USA ND) for workers handling Basamid G. For calculating the exposure rate, the MOEs for applications to a 40-acre field and an application rate of 530 lbs/acre—i.e., at total of 21,200 lbs handled—are used to minimize rounding errors in calculating the exposure rates. Note that the 530 lbs/acre is the application rate used by U.S. EPA/OPP/HED (2009a, p. 75) to derive the MOEs. In Worksheet C01, this application rate is adjusted to the application rate of 350 lbs/acre that will be used by the Forest Service.

As summarized in Worksheet C01, the worker exposures associated with an application rate of 350 lb/acre with 10 acres treated per day range from about 0.0004 mg/kg bw/day (engineering controls) to 0.02 mg/kg bw/day (baseline).

It should be noted that these occupational exposures apply to dazomet rather than methyl isothiocyanate. As discussed in U.S. EPA/OPP/HED (2009a, p. 75), these exposures will be predominantly dermal and will occur prior to the generation of significant amounts of methyl isothiocyanate.

#### *3.2.1.2. Inhalation (Methyl Isothiocyanate)*

As discussed in Section 2, dazomet is rapidly converted to methyl isothiocyanate in soil, and methyl isothiocyanate is primary toxic agent of concern. As summarized in Table 1 and discussed in various U.S. EPA risk assessments, inhalation is the major route of exposure to methyl isothiocyanate (U.S. EPA/OPP 2008a,b; U.S. EPA/OPP/EFED 2008a; U.S. EPA/OPP/HED 2009a).

Workers as well as members of the general public could be exposed to methyl isothiocyanate as this agent volatilizes from soil. The current screening level analysis adopts the exposure assessments from U.S. EPA/OPP/EFED (2008a, p. 37 ff.) using the Industrial Source Complex Short Term (ISCST3) model for a 40-acre field and an application rate of 530 lbs/acre at various wind speeds, distances downwind, and levels of atmospheric stability. Note that the 530 lbs/acre is the application rate used in the EPA modeling rather than the 350 lbs/acre that the Forest Service proposed to use. While not explicitly discussed in U.S. EPA/OPP/EFED (2008a), the atmospheric stability categories appear to be Pasquill Stability Classes which range from extremely unstable (Class A) to moderately stable (Class F) (e.g., https://ready.arl.noaa.gov/READYpgclass.php). As detailed in U.S. EPA/OAQPS (1995) the Industrial Source Complex model is a deterministic dispersion model which can be used to estimate peak/short term concentrations in air (using ISCST3) or longer-term concentrations in air (using ISCLT3). U.S. EPA/OPP/EFED (2008a) estimates only short-term concentrations.

The estimated concentrations of methyl isothiocyanate in air from U.S. EPA/OPP/EFED (2008a, p. 105-106) are summarized in the upper section of Worksheet C02. The lower section of Worksheet C02 normalizes the concentrations based on the values entered in Worksheet A01 for the application rate used by the Forest Service and the size of the treated field. For the current analysis, these values are taken as 350 lb/acre to a 40-acre field. As summarized in Worksheet C02, the modelled concentrations range from 6.83 to about 2770 $\mu g/m^3$.

For the sake of completeness, it is noted that U.S. EPA/OPP/HED (2010a) also uses the Probabilistic Exposure and Risk model for FUMigants (PERFUM) (Reiss and Griffin 2008). As the name indicates, this is a probabilistic rather than deterministic model. The application of the probabilistic method is beyond the scope of the current limited assessment.

In addition to dispersion modelling, U.S. EPA/OPP/HED (2009, p. 69, Table 6.1.4.1) summarizes concentrations of methyl isothiocyanate monitored in California from areas characterized as “high use”. These monitoring data, as reported by EPA, are reproduced in Worksheet B05, and statistics (mean, minimum, and maximum) are summarized in Worksheet E02b of the EXCEL workbook that accompanies this document. As indicated in Worksheet B05, the monitoring data are reported as both maximum and mean concentrations.
For risk characterization, U.S. EPA/OPP/HED (2009, p. 69, Table 6.1.4.1) uses the maximum concentrations to characterize acute risks and the mean concentrations to characterize both short-

term and intermediate-term risks. As detailed further in Section 3.4, the same approach is used in the current analysis.

As indicated in Worksheet B05, the EPA reports the monitoring data as ppm (v/v). As discussed in Section 3.2.2.2, the toxicity data are expressed in units of µg/m$^3$. For all of the analyses in the current document, units of ppm (v/v) are converted to µg/m$^3$ using the following equation:

$$\mu g / m^3 = \frac{24.1 L / mole}{MW} \times ppm(v / v) \times 1000 \mu g / mg \qquad (2)$$

Details of this conversion are given in Drager Safety AG (2011). It should be noted that the constant of 24.1 L/mole is the molar volume of an ideal gas at 20°C or about 68°F. Differing temperatures will require the use of different constants for the molar volume; however, these differences do not have a substantial impact on the conversions. Specifically, the molar volume of a gas is defined (using the Ideal Gas Law) as:

$$V = \frac{R T_K}{P} \qquad (3)$$

where R is the universal gas constant (0.08207 L atm/K mol), $T_K$ is the temperature in Kelvin units (0 °C = 273.15° K), and P is the barometric pressure in units of atmosphers (1 atm = 760 mm Hg). The above equation is simply a rearrangement of the Ideal Gas Law (PV=nRt) where the number of moles (n) is set to 1 (e.g., http://authors.library.caltech.edu/25050/4/Chapter_03.pdf ).

As summarized in Worksheet E02b, the maximum peak concentrations are about 8.5 (0.19-45) µg/m$^3$ and the longer-term average concentrations are about 4.7 (0.03-23) µg/m$^3$. These concentrations are in the lower range of the concentrations modeled using ISCST3 (Worksheet C02)—i.e., distances of about 500 feet or greater from the application site under moderate wind speeds of about 2.5 m/s (≈4.5 mph) or greater, which seems intuitively reasonable given that the monitoring data summarized in U.S. EPA/OPP/HED (2009, p. 69, Table 6.1.4.1) were not sampled at application sites.

[Working Note: Worksheet E02b contains a shaded area near the bottom of the worksheet that implements Equation 2 for converting ppm to µg/m$^3$ using the molecular weight of 73.11 for methyl isothiocyanate and the molar gas volume of 24.1 L/mole. This utility was used in making conversions not otherwise detailed in the text of this document.

To the right of the ppm to µg/m$^3$ conversion tool, the workbook has another utility that implements Equation 3 for calculating the molar volume of a gas at any temperature and barometric pressure.]

The product label for Basamid G indicates that methyl isothiocyanate concentrations may range from 0.6 to 6 ppm may after applications of dazomet. These concentrations correspond to about

1820 to 18,000 µg/m$^3$ (using the above equation). The lower bound of this range is only modestly below the highest concentration of 2770 µg/m$^3$ estimated in Worksheet C02 for or the Forest Service application rate of 350 lb/acre. This is not to suggest a validation of the EPA modeling; however, these relationships do suggest that the modeled concentrations of 6.83 µg/m$^3$ to about 2770 µg/m$^3$ are not implausible.

### 3.2.2. General Public

#### *3.2.2.1. Surface Water (Methyl Isothiocyanate)*

##### 3.2.2.1.1. Expected Concentrations

Full Forest Service risk assessments typically estimate concentrations of a pesticide in surface water using GLEAMS-Driver (SERA 2014, Section 3.2.3.4.3). GLEAMS, however, does not explicitly accommodate soil fumigation (Knisel and Davis 2000). While fumigation might be approximated using soil injection, this type of custom modelling is beyond the scope of the current effort.

As an alternative, the surface water modeling from U.S. EPA/OPP/EFED (2008a) using PRZM/EXAMS is adapted to the current assessment. As with GLEAMS, PZMZ/EXAMS has limitations in terms of handling highly volatile compounds in soil that are addressed in U.S. EPA/OPP/EFED (2008a, p. 9) in a reasonably conservative manner. U.S. EPA/OPP/EFED (2008a, p. 30-31) provides five application scenarios: two in California (tomatoes and strawberries), two in Florida (both turf), and one in Oregon (Christmas trees). Because the current assessment is focused on a Forest Service nursery in Oregon, the results from the Oregon scenario are used in the current assessment (i.e., U.S. EPA/OPP/EFED 2008a, p. 103). The peak (lower bound – upper bound) concentrations from the EPA analysis are 0.00033 (0.00001 to 0.00064 mg/L) and the 90-day average concentrations are 0.00002 (0.00001 to 0.00004) mg/L. The central and upper bound estimates are based on the average and maximum concentrations reported in U.S. EPA/OPP/EFED (2008a, p. 103). Many of the yearly concentrations reported by EPA are zero, which is similar to many GLEAMS-Driver simulations in Forest Service risk assessments. Consequently, the lower bounds are set at the lowest non-zero concentrations reported. The EPA simulations were done at a maximum application rate of 530 lb/acre (U.S. EPA/OPP/EFED 2008a, p. 32, Table III.b).

The concentrations reported by EPA were thus normalized to Water Contamination Rates (WCRs, in units of mg/L per lb/acre) by dividing the values by the application rate of 530 lb/acre. Details of these calculations are given in Worksheet B04Rt of the EXCEL workbook that accompanies this risk assessment. As discussed in SERA (2014, 3.2.3.4.6), the WRCs are multiplied by the application rate of 350 lbs/acre in Worksheet A01 to estimate the expected concentrations of methyl isothiocyanate in water, which are given in Worksheet B04a.

The estimated concentrations of methyl isothiocyanate in surface water are used to elaborate exposure scenarios associated with acute exposure scenarios (Worksheets D05, D09a, D09b, and D11), and longer-term exposure scenarios (D07, D-09a, and D09b). These are standard exposure scenarios used in most Forest Service risk assessments as detailed in SERA (2014). As discussed in Section 3.3.1, dietary exposures are not relevant given the application method and properties of methyl isothiocyanate.

#### 3.2.2.1.2. Accidental Spill

Accidental spill scenarios are considered in most Forest Service risk assessments and typically model spills of 100 (20-200) gallons of a field solution. This type of scenario, however, is not relevant to applications of dazomet. As an alternative, an accidental spill scenario is developed in Worksheet B04b involving a dazomet spill in the amount used to treat 0.1 (0.01 to 1) acre. At the application rate of 350 lb/acre used in the WorksheetMaker workbook that accompanies this assessment, the spill is equivalent to 35 (3.5 to 350) lbs of dazomet. Because of the rapid conversion of dazomet to methyl isothiocyanate, the expected concentrations are converted to units of methyl isothiocyanate by multiplying the mass of dazomet by the ratio of the molecular weight of methyl isothiocyanate (73.11 g/mole) to the molecular weight of dazomet (162.27 g/mole). The estimated concentrations of dazomet in surface water following an accidental spill are detailed in Worksheet B04b.

The values for estimated concentrations of dazomet in surface water following an accidental spill are simply intended to reflect central (lower bound to upper bound) spills that might reasonably be viewed as moderate (small to large). The accidental spill scenarios are detailed in Worksheets D05 (consumption of water by a small child), D08a (consumption of contaminated fish by a member of the general population), and D08b (consumption of contaminated fish by a member of a subsistence population).

#### *3.2.2.2. Inhalation*

The approach to handling inhalation exposures to methyl isothiocyanate by members of the general public is identical to that used for workers (Section 3.2.1.2). The only difference is that workers are likely to be closer than the general public to the treated field, as discussed in the risk characterization for members of the general public (Section 3.4.2.2).

## 3.3. Dose-Response Assessment

The toxicity values for dazomet and methyl isothiocyanate relating to potential health effects in humans are summarized in Table 2 and are discussed below. The toxicity values summarized in Table 2 are based on the most recent EPA human health risk assessment (U.S. EPA/OPP/HED 2009a).

### 3.3.1. Dazomet

RfDs or comparable values for dazomet have been proposed by the European Food Safety Authority (ESFA 2010) and the U.S. EPA/OPP's Health Effects Division (U.S. EPA/OPP/HED 2009a). It should be noted that both sets of toxicity values are consistent with each other and appear to be based on the same studies. The major difference between the two sets of values is that the U.S. EPA did not perceive a need for any chronic oral toxicity values for dazomet because it is rapidly converted to methyl isothiocyanate. The current assessment agrees with the EPA position. The chronic RfD is noted for the sake of completeness but is not used quantitatively in the EXCEL workbook that accompanies this risk assessment.

The toxicity values from U.S. EPA/OPP/HED (2009a) are presented solely for the risk assessment of workers by dermal exposures:

> *Based on the currently registered use pattern of dazomet, dietary exposure is not expected. Acute and chronic reference doses are not necessary at this time.*

U.S. EPA/OPP/HED (2009a, p. 16).

Again, this approach is sensible. Given the rapid conversion of dazomet to methyl isothiocyanate, exposures of members of the general public to dazomet should be minimal and insignificant, relative to exposures to methyl isothiocyanate.

Note that most of the exposure assessments (Section 3.2) involve methyl isothiocyanate. The only exception involves workers applying dazomet. Consistent with the approach used in U.S. EPA/OPP/HED (2009), the assumption is made that workers applying dazomet will be exposed primarily to dazomet rather than methyl isothiocyanate. Thus, the only toxicity value for dazomet used quantitatively in the EXCEL workbook is 0.015 mg/kg bw/day which is adopted from U.S. EPA/OPP/HED (2009a, p. 28) and consistent with the occupational exposure limit recommended by ESFA (2010, p. 7) and the European Union (2012, p. 3).

### 3.3.2. Methyl Isothiocyanate (MITC)

Both oral RfDs (or their equivalents such as Acceptable Daily Intakes [ADIs] and Acceptable Occupational Exposure Limits [AOELs]) as well as RfCs (Reference Concentrations) or analogous values are available on methyl isothiocyanate.

#### *3.3.2.1. Oral Toxicity Values*

The oral acute RfD and chronic ADI are given in the risk assessment by European Food Safety Authority (ESFA 2010). The U.S. EPA/OPP assessments on dazomet and methyl isothiocyanate do not derive oral or dermal toxicity values for methyl isothiocyanate, because significant oral or dermal exposures were not anticipated in the EPA assessments (e.g., U.S. EPA/OPP/HED 2009a, p. 22).

As discussed in Section 3.2.2.1, however, the EPA's most recent ecological risk assessment on dazomet does estimate concentrations of methyl isothiocyanate in surface water (U.S. EPA/OPP/EFED 2008a). When concentrations of a compound in surface water can be estimated, Forest Service risk assessments will use these estimates for risk characterization so long as adequate toxicity data are available. The European Food Safety Authority is a credible organization, and the acute and chronic oral toxicity values from EFSA (2010) are accepted without modification. These toxicity values, specified in Table 2, are used to characterize risks associated with the acute and longer-term consumption of surface water contaminated with methyl isothiocyanate.

#### *3.3.3.2. Inhalation Toxicity Values*

The EPA derived inhalation toxicity values for acute exposures to methyl isothiocyanate (U.S. EPA/OPP/HED 2009a, pp. 18-20). Somewhat atypically, the EPA derived two sets of acute toxicity values, one for eye irritation in humans and the other for systemic toxicity.

The toxicity value for eye irritation is based on a human study on eye irritation and odor threshold over exposure periods of 4 minutes to 8 hours (U.S. EPA/OPP/HED (2009a, pp. 17-19, MRID 44400401). For exposure periods of 1 to 8 hours, the NOAEL was designated as 0.22 ppm (U.S. EPA/OPP/HED 2009a, Table 4.4e, p. 29). Because this study is based on human data, the EPA used an uncertainty factor of 10 to account for potential variability within the human population. Thus, the acute toxicity value—i.e., a functional acute RfD—is 0.022 ppm or

approximately 66.7 µg/m$^3$. In the EXCEL workbook that accompanies this document, a utility included at the bottom of Worksheet E02b may be used for converting ppm to µg/m$^3$.

For short- and intermediate-exposures (1 day to 6 months), the toxicity value is 0.166 mg/m$^3$ (166 µg/m$^3$). The concentration of 0.166 mg/m$^3$ is based on the NOAEL of 5 mg/m$^3$ from a 28-day inhalation study in rats exposed to methyl isothiocyanate nominal concentrations 0, 5, 20, or 100 mg/m$^3$ (U.S. EPA/OPP/HED 2009a, pp. 82-83, MRID 45314802). At 20 mg/m$^3$, adverse effects included an increase in a type of white blood cell (i.e., neutrophilic polymorphonuclear granulocytes) as well as clinical signs consistent with irritation. The EPA did not specifically derive an RfC but used the NOAEL of 5 mg/m$^3$ with a margin of exposure of 30, which is equivalent to setting the subchronic RfC at 0.166 mg/m$^3$ [5 mg/m$^3$ ÷ 30 ≈ 0.166 mg/m$^3$] (U.S. EPA/OPP/HED 2009a, Table 4.4e, p. 29).

## 3.4. Risk Characterization

### 3.4.1. Workers

#### *3.4.1.1. Applications (Dazomet)*

The HQs for workers are given in Worksheet E01 of the EXCEL workbook. These HQs range from 1.3 (i.e., baseline or no PPE) to 0.03 (i.e., full PPE/engineering controls). Given the detailed description of worker PPE provided by the Forest Service and the requirements specified on the product label (Section 3.2.1.1), the HQ of 0.03 is clearly the only HQ relevant to the current assessment. This HQ is below the level of concern (HQ=1) by a factor of over 30. Thus, there is no basis for asserting that workers will be at risk of adverse effects associated with applications of dazomet.

#### *3.4.1.2. Inhalation (Methyl Isothiocyanate)*

The HQs for acute eye irritation for exposure to air concentrations of methyl isothiocyanate are given in Worksheet E02a. The HQs in Worksheet E02a would not apply to workers during the application of dazomet, due to the use of protective clothing, including respirators. After applications, however, workers could be in the area of the treated soil and exposed to methyl isothiocyanate vapors.

As summarized in Worksheet E02a, the HQs are highly variable ranging from about 0.1 to 42. These HQs are based on a concentration of 66.7 µg/m$^3$ for eye irritation (Section 3.3.3.2) and air concentrations estimated by the EPA under a variety of winds speeds, atmospheric stability, and distances downwind (U.S. EPA/OPP/EFED 2008a), as discussed in Section 3.2.1.2. As summarized in Table 2, the concentration of 66.7 µg/m$^3$ is based on an uncertainty factor of 10, a human NOAEL of 66.7 µg/m$^3$ associated with a human LOAEL of 2392 µg/m$^3$ for eye irritation. Thus, an HQ of 10 would correspond to the reported human NOAEL and an HQ of about 36 would correspond to the observed human LOAEL [2392 µg/m$^3$ ÷ 66.7 µg/m$^3$ ≈ 35.86].

For workers on or very close to the application site, HQs in the range of 10 to 40 could be applicable at low wind speeds and under relatively stable atmospheric conditions on the application site (i.e., no buffer). Eye irritation could not be ruled out in some workers who are sensitive to methyl isothiocyanate. Conversely, under less extreme conditions, it is plausible that

no signs of eye irritation would be noted in workers or other individuals in the area of the application site.

The duration of potential risks due to vapor release cannot be determined based on the modeling done by EPA. As discussed further in Section 3.4.2.2, the product label for Basamid G specifies a 48-hour period in which a buffer zone must be in effect, which suggests that vapor release after 48 hours may be negligible. U.S. EPA/OPP/HED (2009a), however, does not explicitly discuss the rationale for the 48-hour buffer period specified on the Certis product label.

### 3.4.2. General Public

#### *3.4.2.1. Surface Water*

The risk characterization associated with exposures to methyl isothiocyanate in surface water is given in Worksheet E04. Based on the estimated concentrations of methyl isothiocyanate in surface water (Section 3.2.2.1.1), none of the HQs approach a level of concern (HQ=1). The highest HQ is 0.002, the upper bound for the short-term consumption of contaminated water by a small child. This HQ is below the level of concern by a factor of 500.

In the event of an accidental spill (Section 3.2.2.1.2), all of the central and upper estimates of the HQs exceed the level of concern ranging from 1.7 to 269. As discussed in Section 3.2.2.1.2, this exposure scenario is based on variable assumptions involving the amount spilled—i.e., 35 (3.5 to 350) lbs of dazomet. The HQs for this exposure scenario simply suggest that mitigation measures would be appropriate in the event of an accidental spill of dazomet into a relatively small body of water. This risk characterization is similar to that of many accidental spill scenarios considered in full Forest Service risk assessments.

#### *3.4.2.2. Inhalation*

The risk characterization for inhalation exposures for members of the general public can be based on the modeling from U.S. EPA/OPP/EFED (2008a) and the monitoring data reported in U.S. EPA/OPP/HED (2009a).

The product label for Basamid G (Certis USA, ND) specifies buffer zones for different types of applications of dazomet and specifies that the buffer zone must remain in effect for 48 hours. Based on Table 1 of the product label, the buffer zone for an application rate of about 350 lb/acre to a 40-acre field is about 680 feet. The Forest Service has indicated, however, that only 10 acres would be treated in a given day and that the typical buffer would be about 220 feet (Justin 2014). This buffer is consistent with the product label for Basamid G (Certis USA, ND) for field size of 10 acres and an application rate of about 350 lb/acre.

Thus, the HQs in Worksheet E02a for 0 to 200 feet downwind would not be applicable to members of the general public. Excluding these HQs results in HQs for the general public that range from 0.1 to 10. The HQs that exceed the level of concern by a factor of 2 or more are those for low wind speeds (≈1 m/s or about 2.2 mph) and relatively stable atmospheric conditions (stability categories F and D). These HQs range from 2 to 10 and. These HQs might be associated with eye irritation in some sensitive members of the population.

In addition to the modeled estimates of methyl isothiocyanate in air from U.S. EPA/OPP/EFED (2008a), risks to both workers and members of the general public can be estimated from the monitoring provided in U.S. EPA/OPP/HED (2009a). These data are summarized in Worksheet B02b. As with the analysis in U.S. EPA/OPP/HED (2009a, Table 6.1.4.1, p. 69), risks associated with the maximum concentrations are characterized using the concentration of 66.7 $\mu g/m^3$ based on eye irritation, and risks associated with the mean concentrations are characterized using the concentration of 167 $\mu g/m^3$ based on systemic effects (i.e., an increase in white blood cells). As summarized in Worksheet E02b, none of the HQs exceed the level of concern (HQ=1) with the acute HQs ranging up to 0.7 and the intermediate-term HQs (i.e., for 1 day to 6 months) ranging up to 0.1.

# 4. ECOLOGICAL EFFECTS

## 4.1. Hazard Identification

As with the hazard identification for human health (Section 3.2), the hazard identification for ecological effects is highly abbreviated in the current document. The overall database for ecological effects is discussed in detail in U.S. EPA/OPP/EFED (2008a), the most recent risk assessment on dazomet as well as the EPA's final work plan for the registration review of dazomet (U.S. EPA/OPP 2014). The current assessment relies heavily on U.S. EPA/OPP/EFED (2008a) for the derivation of HQs. As detailed in these EPA documents, there are several important data gaps for methyl isothiocyanate. These data gaps have an impact on the risk characterization for methyl isothiocyanate as discussed further in Section 4.4.

## 4.2. Exposure Assessment

### 4.2.1. Oral

#### *4.2.1.1. Dazomet*

Given the application method for dazomet—i.e., soil incorporation—most of the standard oral exposure scenarios (e.g., consumption of contaminated vegetation) used in both EPA and Forest Service risk assessments are not applicable to dazomet. In addition and as discussed in Section 2, dazomet is rapidly converted to methyl isothiocyanate. Some relevant oral exposure scenarios for methyl isothiocyanate are discussed in Section 4.2.1.2.

U.S. EPA/OPP/EFED (2008a) uses an $LD_{50}$/square foot method as a screening tool. As the name implies, this method involves calculating the amount of the pesticide applied to a square foot and comparing this to a relevant $LD_{50}$. This is a convention developed by the U.S. EPA as a screening tool and is not directly used in the current risk assessment.

As noted in Section 1.2, the application rate anticipated by the Forest Service is 350 lbs/acre, which corresponds to approximately 3600 $mg/ft^2$ [350 lbs/acre x 453,592 mg/lb ÷ 43,560 $ft^2$/acre ≈ 3,644.5638 $mg/ft^2$]. As discussed further in Section 4.3.1, the $LD_{50}$ values for mammals and birds are somewhat greater than 400 mg/kg bw. For a small (200 g) mammal, this value corresponds to a dose of 80 mg. Thus, an application rate of 350 lbs/acre would involve about 45 $LD_{50}$ values per square foot [3600 $mg/ft^2$ ÷ 80 $mg/LD_{50}$].

The above relationships are noted solely in the interest of transparency. While these types of relationships may be useful to the EPA as a screening tool, they are not relevant to assessing risks associated with soil incorporation. As detailed in Section 3.2.1.1, the manner in which dazomet is applied in Forest Service programs—i.e., soil application followed immediately by tilling and watering in—will greatly limit any exposure of mammals or birds to dazomet. Consequently, no oral exposure scenarios for dazomet are developed in the EXCEL workbook that accompanies this risk assessment.

##### *4.2.1.1. Methyl Isothiocyanate*

As with standard Forest Service risk assessments, exposure assessments associated with both expected concentrations of methyl isothiocyanate in surface water and concentrations in surface water following an accidental spill are identical to those used in the assessment of potential effects in humans (Section 3.2.2.1). The only differences involve the amount of water consumed by different groups of vertebrates. The specific assumptions used for estimating doses associated with the consumption of contaminated surface water are detailed in Table 17 of SERA (2014). The estimated doses for mammals and birds are summarized in Worksheet G01a (mammals) and G01b (birds) of the EXCEL workbook that accompanies this document. These summary worksheets reference the worksheets in which each exposure scenario is detailed.

### 4.2.2 Inhalation

Wildlife may be exposed to methyl isothiocyanate in the air. The estimated concentrations of methyl isothiocyanate in air used to assess effects in wildlife are identical to those used to assess exposures in workers. As detailed in the exposure assessment for workers (Section 3.2.1.2), these concentrations are adopted from the EPA ecological risk assessment for dazomet (U.S. EPA/OPP/EFED 2008a). The specific concentrations are summarized in Worksheet C02.

Furthermore, like the assessment of inhalation exposures to humans, inhalation risks to wildlife are assessed based on monitoring data from U.S. EPA/OPP/HED (2009a, Table 6.1.4.1). These monitoring data are summarized in Worksheet B05.

## 4.3. Dose-Response Assessment

The dose response assessment for nontarget organisms is summarized in Table 3 and is discussed in the following subsections on different groups of receptors.

### 4.3.1. Terrestrial Organisms

#### *4.3.1.1. Mammals*

##### 4.3.1.1.1. Dazomet

As discussed in Section 4.2.1.1, substantial exposures of mammalian wildlife to dazomet are unlikely, given the manner in which dazomet is applied. As discussed in Section 4.2.1.1, U.S. EPA/OPP/EFED (2008a) uses an $LD_{50}$/square foot method as a screening approach. This approach is based on a standard $LD_{50}$ of 415 mg/kg bw in rats. In the interest of transparency, it is noted that this method triggers concern for all risk categories used by the U.S. EPA, as detailed in Table IV.i. in U.S. EPA/OPP/EFED (2008a, p. 49). As noted in Section 4.2.1.1, however, the $LD_{50}$ per square foot approach is a screening tool developed by the U.S. EPA/OPP and is not directly relevant to the current assessment.

#### 4.3.1.1.2. Methyl Isothiocyanate

While exposures of mammalian wildlife to dazomet are unlikely, potential oral and inhalation exposures to methyl isothiocyanate are plausible.

As discussed in Section 3.3.2.1 and summarized in Table 2, the acute oral RfD is based on an NOAEL of 3 mg/kg bw from a reproduction study in rats. Following standard practice in Forest Service risk assessments (SERA 2014), the basis for the human health risk assessment is used as the basis for assessing effects in mammalian wildlife. Thus, the NOAEL of 3 mg/kg bw is used to characterize risks to mammals following short-term oral exposures to methyl isothiocyanate. Similarly, the NOAEL of 0.4 mg/kg bw/day in dogs (which is the basis for the chronic oral RfD) is used to assess the consequences of longer-term oral exposures of mammalian wildlife to methyl isothiocyanate.

For inhalation exposures, the intermediate NOAEL of 5 mg/m$^3$ from the 28-day study in rats (U.S. EPA/OPP/HED 2009a, pp. 82-83, MRID 45314802) is used to assess intermediate inhalation exposures. While this study is used by U.S. EPA/OPP/HED (2009a) to assess both acute and intermediate exposures in humans, the use of the 5 mg/m$^3$ 28-day NOAEL is not appropriate for assessing short-term exposures in mammalian wildlife. As an alternative, the acute $LC_{50}$ of 540 mg/m$^3$ in rats (MRID 45919410 as summarized in U.S. EPA/OPP/EFED 2008a, p. 110) is divided by a factor of 10 to approximate an acute NOAEL of 54 mg/m$^3$. The rationale for the estimation of a NOAEL from an $LD_{50}$ is discussed in SERA (2014, Section 4.3.2) and is a modification of the methods used by U.S. EPA/OPP for defining variable levels of concern.

### *4.3.1.2. Birds*

#### 4.3.1.2.1. Dazomet

As with mammals (Section 4.2.1.1), substantial exposures of avian wildlife to dazomet are unlikely, given the manner in which dazomet is applied. Also, as with mammals, U.S. EPA/OPP/EFED (2008a) uses an $LD_{50}$/square foot method as a screening approach to assess potential effects in avian wildlife. This approach is based on a standard $LD_{50}$ of 424 mg/kg bw in bobwhite quail (U.S. EPA/OPP/EFED 2008a, MRID 423651, p. 56). This $LD_{50}$ is almost identical to the $LD_{50}$ of 415 mg/kg bw in rats. Consequently, the $LD_{50}$/square foot method triggers concern for all risk categories used by the U.S. EPA, as detailed in Table IV.h. in U.S. EPA/OPP/EFED (2008a, pp. 48-49). As with the use of the $LD_{50}$/square foot method for mammals, this EPA screening method is not directly relevant to the current analysis.

Reproduction studies have been submitted for both mallard ducks (MRID 43245001) and bobwhite quail (MRID 43245002). The EPA considers these studies not relevant to risk assessment because they do not define clear NOAELs and LOAELs. U.S. EPA/OPP/EFED (2008a, p. 108) notes that *…birds may be subject to repeated or continuous exposure to the pesticide, especially preceding or during the breeding season*. The EPA, however, does not detail the plausible exposure scenarios for soil incorporation considering the rapid conversion of dazomet to methyl isothiocyanate. U.S. EPA/OPP/EFED had adequate toxicity data to develop a subchronic assessment of dazomet in mammals but elected to consider only acute exposures to dazomet (U.S. EPA/OPP/EFED 2008a). Thus, it is not clear how or if EPA would have assessed longer-term risks to birds if adequate toxicity studies were available.

#### 4.3.1.2.2. Methyl Isothiocyanate

No inhalation toxicity data in birds are available for methyl isothiocyanate. This is a concern because birds could be at greater risk than mammals due to physiological differences in the lung structure of birds and mammals (U.S. EPA/OPP/EFED 2008a, p. 4). While the EPA does not specifically discuss these differences, the discussion probably refers to the reciprocating ventilation system of mammals and the flow-through ventilation system of birds (e.g. Powell and Hopkins 2003; West et al. 2007).

#### *4.3.1.3. Other Terrestrial Organisms*

An acute contact $LD_{50}$ of >24 µg/bee is available for dazomet. This toxicity value is not directly relevant to the risk assessment of dazomet because the application method will not lead to contact exposures in honeybees (U.S. EPA/OPP/EFED 2008a, p. 53). Relevant toxicity data to other groups of nontarget terrestrial organisms have not been identified. As also noted in U.S. EPA/OPP/EFED (2008a, p. 53), this is a concern because methyl isothiocyanate is an effective biocide and it is likely to adversely affect nontarget soil invertebrates in treated soil.

One of the reasons for applying dazomet is for the control of unwanted vegetation due to the phytotoxicity of methyl isothiocyanate. No standard toxicity studies in terrestrial plants, however, were submitted to the EPA (U.S. EPA/OPP/EFED 2008a, p. 44).
No studies on the toxicity of dazomet or methyl isothiocyanate to terrestrial phase amphibians or reptiles have been encountered. In ecological risk assessments prepared by U.S. EPA/OPP, birds are commonly used as surrogates for terrestrial phase amphibians and reptiles (e.g. U.S. EPA/OPP/EFED 2008a, p. 38). A concern with the use of birds as a surrogate for amphibians involves the permeability of amphibian skin to pesticides and other chemicals. Quaranta et al. (2009) noted that the skin of the frog *Rana esculenta* is much more permeable to several pesticides, relative to pig skin, and that these differences in permeability are consistent with differences in the structure and function of amphibian skin, relative to mammalian skin.

### 4.3.2. Aquatic Organisms

U.S. EPA/OPP/EFED (2008a) does not discuss the toxicity of dazomet to aquatic organisms because dazomet will be rapidly hydrolyzed to methyl isothiocyanate in water (Section 2). Consequently, all toxicity values discussed below refer to methyl isothiocyanate.

#### *4.3.2.1 Fish*

Data on the toxicity of methyl isothiocyanate to fish consists of two 96-hour $LC_{50}$ values—i.e., 0.094 mg/L for rainbow trout (MRID 44523412) and 0.142 mg/L for bluegill sunfish. Based on the $LC_{50}$ values, methyl isothiocyanate is classified as *highly toxic* to fish. NOAEC values associated with these $LC_{50}$ values are not reported in U.S. EPA/OPP/EFED (2008a, p. 40).

As summarized in Table 3, the $LC_{50}$ values are divided by 20 to approximate NOAECs. The rationale for approximating an NOAEC from an $LD_{50}$ is discussed in SERA (2014, Section 4.3.2). While the $LC_{50}$ values for trout and bluegills are not remarkably different from each other, the somewhat lower estimated NOAEC in trout is used to characterize acute risks to sensitive species and the estimated NOAEC in bluegills is used to characterize acute risks to tolerant species.

The EPA notes that a …*non-guideline 28-day subchronic study*… in rainbow trout was submitted to the Agency (MRID 45634002) but that this study is classified as invalid because the concentrations of methyl isothiocyanate in the test waters were not *adequately assessed* (U.S. EPA/OPP/EFED 2008a, p. 39). Consequently, longer-term risks to fish are not quantitatively characterized.

#### *4.3.2.2. Aquatic Invertebrates*

Two studies are available on the toxicity of methyl isothiocyanate to *Daphnia magna*—i.e., an acute $EC_{50}$ of 0.055 mg/L (MRID 41819302) and a 21-day reproduction NOAEC of 0.025 mg/L (MRID 4563401) (U.S. EPA/OPP/EFED 2008a, p. 39). Typically, the $EC_{50}$ of 0.055 mg/L would be divided by a factor of 20 to approximate an acute NOAEC (SERA 2014, Section 4.3.2). This procedure would estimate an acute NOAEC of 0.00275 mg/L [0.055 mg/L ÷ 20]. Given the chronic NOAEC of 0.025 mg/L, however, the approximation of a 0.00275 mg/L acute NOAEC would not be sensible. Consequently, the chronic NOAEC of 0.025 mg/L is used to characterize risks associated with both acute and longer-term exposures to methyl isothiocyanate in surface water.

Because data are available on only *Daphnia magna*, the assumption is made that *Daphnia magna* is a tolerant species and that data on potentially sensitive species are not available. While this assumption may be viewed as conservative, it is a standard approach in Forest Service risk assessments.

#### *4.3.2.3. Aquatic Plants*

##### 4.3.2.3.1. Algae

$EC_{50}$ values are available for three species of algae: *Anabaena flos-aquae* ($EC_{50}$ = 1.5 mg/L based on cell density from MRID 45919422), *Selenastrum capricornutum* ($EC_{50}$ = 0.28 mg/L with a NOAEC of 0.207 mg/L based on biomass from MRID 45919416), and *Scenedesmus subspicatus* ($EC_{50}$ = 0.254 mg/L based on cell density from MRID 44588903).

As discussed in previous sections, one approach to estimating a NOAEC from an $LC_{50}$ or $EC_{50}$ in aquatic species is to divide the $LC_{50}$ or $EC_{50}$ by 20 (SERA 2014, Section 4.3.2). This approach is a default in the absence of other data. For methyl isothiocyanate, both an $EC_{50}$ and an NOAEC are available in *Selenastrum capricornutum*. While this species is not the most sensitive or most tolerant species, the ratio of the NOAEC to the $LC_{50}$ [0.207 ÷ 0.28 ≈ 0.74] can be used as an adjustment factor for estimating the NOAEC from the $EC_{50}$ values in other species of algae. Using this approach, the NOAEC for the most sensitive species, *Scenedesmus subspicatus*, is estimated as 0.19 mg/L [0.254 mg/L x 0.74]. Similarly, the NOAEC for the most tolerant species, *Anabaena flos-aquae*, is estimated as 1.1 mg/L [1.5 mg/L x 0.74].

##### 4.3.2.3.2. Aquatic Macrophytes

Only one study is noted in U.S. EPA/OPP/EFED (2008a, p. 114) for an aquatic macrophyte—i.e., an $EC_{50}$ in *Lemna gibba* of 0.59 mg/L based on frond number with a corresponding NOAEC of 0.09 mg/L (MRID 459 19421). In the absence of additional information, the assumption is made that *Lemna gibba* is a tolerant species and that toxicity data on a more sensitive species have not been identified. Thus, for characterizing risks to aquatic macrophytes, the NOAEC of 0.09 mg/L is used and applied to the risk characterization for tolerant species.

#### *4.3.2.4. Other Aquatic Organisms*

No data have been encountered on the toxicity of methyl isothiocyanate to aquatic phase amphibians or aquatic microorganisms. As noted in U.S. EPA/OPP/EFED (2008a, p. 38), toxicity data on fish are used as a surrogate for aquatic-phase amphibians. This is a standard practice in EPA ecological risk assessments. U.S. EPA/OPP/EFED (2008a) does not address potential effects in aquatic microorganisms other than algae (Section 4.3.2.3.1).

## 4.4. Risk Characterization

### 4.4.1. Terrestrial Organisms

#### *4.4.1.1. Mammals*

The risk characterization for mammals is summarized in Worksheet G02a (oral exposures to methyl isothiocyanate in surface water), Worksheet G04a (inhalation exposures to methyl isothiocyanate based on modeling), and Worksheet G04b (inhalation exposures to methyl isothiocyanate based on monitoring).

The only HQs that exceed the level of concern (HQ=1) involve the accidental spill of dazomet into a small body of water. The upper bound HQs for this scenario range from 1.5 (a large mammal) to 18 (a canid consuming contaminated fish). As discussed in Section 3.2.2.1.2, this scenario is based on spills of 35 (3.5 to 350) lbs of dazomet. In an actual spill, greater or lesser concentrations might occur depending on the amount of the spill and the size of the waterbody.

Based on expected concentrations of methyl isothiocyanate in surface water, all of the HQs (Worksheet G02a) are far below the level of concern—i.e., the highest HQ is 0.0001, below the level of concern by a factor of 10,000. While there are uncertainties in the application and suitability of the EPA surface water modeling relative to site-specific modeling that could be conducted, it does not seem likely that site-specific modeling would substantially alter the risk characterization for mammals.

Based on HQs associated with EPA's Industrial Source Complex Short Term (ISCST3) model for a 40-acre field (Section 3.2.1.2), all of the HQs (Worksheet G04a) are below the level of concern based on the estimated acute inhalation NOAEL of 54 $mg/m^3$ (Table 3). The highest HQ is 0.05, below the level of concern by a factor of 20.

Based on HQs associated with the monitoring data summarized in U.S. EPA/OPP/HED (2009a, as discussed in Sections 3.2.2.2 and 4.2.2), all of the HQs (Worksheet G04b) are below the level of concern based both the estimated acute inhalation NOAEL of 54 $mg/m^3$ and the intermediate inhalation NOAEL of 5 $mg/m^3$ (Table 3). The upper bound acute HQ is 0.015, below the level of concern by a factor of about 66. The upper bound HQ for longer-term exposures is 0.005, below the level of concern by a factor of 200.

As discussed in Section 4.2.1.1, U.S. EPA/OPP/EFED (2008a) uses an $LD_{50}$/square foot method as a screening tool, and this analysis triggers concern based on potential exposures to dazomet for all risk categories used by the U.S. EPA, as detailed in Table IV.i. of U.S. EPA/OPP/EFED (2008a, p. 49). Given the manner in which the Forest Service applies dazomet (Section 3.2.1.1), the $LD_{50}$/square foot method does not appear to be pertinent to Forest Service applications.

#### *4.4.1.2. Birds*

Given the lack of toxicity data on the effects of methyl isothiocyanate in birds, no risk characterization for methyl isothiocyanate is proposed.

As with mammals, U.S. EPA/OPP/EFED (2008a) uses an $LD_{50}$/square foot method as a screening tool, and this method triggers concern based on potential exposures to dazomet for all risk categories used by the U.S. EPA. As with mammals, the $LD_{50}$/square foot method does not appear to be pertinent to the risk characterization for birds, given the manner in which Forest Service applications of dazomet are made (Section 3.2.1.1).

#### *4.4.1.4. Other Organisms and Indirect Effects*

As summarized in U.S. EPA/OPP/EFED (2008a, Table IV.k, p. 60), the EPA notes the need for chronic toxicity data in mammals, birds, terrestrial phase amphibians, and reptiles. In addition, potential risks to all groups of terrestrial organisms due to secondary effects are considered possible. This risk characterization is noted in the interest of transparency. Given the limited uses of dazomet in Forest Service programs (Section 1.1.2) as well as the application method for dazomet used in Forest Service programs (Section 3.2.1.1), the applicability of the risk characterization given by the EPA to Forest Service programs is unclear.

### 4.4.2. Aquatic Organisms

The risk characterization for aquatic organisms is summarized in Worksheet G03. The risk characterization is essentially identical for fish, aquatic invertebrates, and aquatic plants. Based on the available information, adverse effects would be expected in all groups of organisms in the event of an accidental spill. The greatest HQs for accidental exposures are associated with fish and range from about 100 (lower bound HQ for tolerant species) to over 15,000 (upper bound HQ for sensitive species).

Based on expected concentrations of methyl isothiocyanate in water, however, all HQs are substantially below the level of concern. The highest acute HQ is 0.09 (the upper bound HQ for sensitive species of fish) and the highest longer-term HQ is 0.001 (the upper bound HQ for aquatic invertebrates).

No toxicity data are available on aquatic phase amphibians; thus, no risk characterization is proposed for this group of organisms.

As is the case with terrestrial organisms, U.S. EPA/OPP/EFED (2008a, Table IV.k, p. 60) indicates concern for all groups of aquatic organisms in terms of the potential for indirect effects. Also, as summarized in Table 3 and discussed in Section 4.3.2 of the current document, no toxicity values are available for several groups of aquatic organisms, particularly in terms of chronic effects and effects in potentially sensitive species. These data gaps add substantial uncertainty to the risk characterization for aquatic organisms. Conversely, as with terrestrial organisms, it seems reasonable to suggest that the limited use of dazomet in Forest Service programs would limit the potential for substantial and extensive adverse effects in aquatic organisms.

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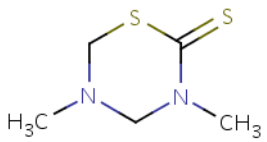
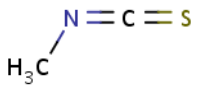
**Table 1: Chemical and Physical Properties**

| Item | Dazomet | Methyl isothiocyanate | Reference[1] |
|---|---|---|---|
| Common name: | Dazomet | Methyl isothiocyanate | ChemIDplus 2014a,b |
| CAS Name | tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione | N/A | Tomlin 2004 |
| CAS No. | 533-74-4 | 556-61-6 | ChemIDplus 2013a,b |
| Chemical Group | dithiocarbamate | isothiocyanate | U.S. EPA/OPP/EFED 2008a |
| EPA PC Code | 035602 | 068103 | Kegley et al. 2014a,b |
| Smiles Code | `N1(C(SC[N@@](C1)C)=S)C` | CN=C=S | ChemIDplus 2013a,b |
| | `S=ClN(CN(CS 1)C)C` | | U.S. EPA/OPP/EFED 2008a |
| | `CN1CSC(=S)N(C)C1` | | Tomlin 2004 |
| Structure |  |  | ChemIDplus 2013a,b |
| | **Chemical Properties**(1) | | |
| Aqueous photolysis, $t_{½}$ | 4 hours at pH7<br>Major degradate: methyl isothiocyanate. | 51.6 days | U.S. EPA/OPP/EFED 2008a, p. 26, MRIDs 414799-01 and 421114-02.;<br><br>CDPR 2002a |
| Photodegradation in air | | 1.21 to 1.6 days | U.S. EPA/OPP/EFED 2008a, p. 27 citing Geddes et al. 1995 |
| Boiling point | | 119 °C | ChemIDplus 2013b |
| Henry's Law Constant | $4.98 \times 10^{-10}$ atm-m$^3$/mole | $4.48 \times 10^{-5}$ atm-m$^3$/mole | ChemIDplus 2013a,b |
| Hydrolysis | **$DT_{50}$ (hours) / pH at 25°C**<br>6.6 / 3<br>6.8 / 4<br>5.8 / 5<br>4.0 / 7<br>4.4 / 7<br>2.8 / 9<br>5.4 / 9<br>Major degradate: methyl isothiocyanate. | **$DT_{50}$ (days) / pH at 25°C**<br>3.5 / 5<br>20.4 / 7<br>4.6 / 9 | U.S. EPA/OPP/EFED 2008a, p. 26, MRIDs 459083-01, 414790-03, and 421 114-01;<br><br>U.S. EPA/OPP/EFED 2008a, p. 27, MRID 00158162 |
| $K_{ow}$ | 19.9 [log Kow = 1.3] | 8.7 [estimate log Kow=0.94] | ChemIDplus 2013a,b |
| | 8.7 [estimate log Kow=0.94]<br>4.3 [experimental log Kow = 0.63] | 20 [estimate log $K_{ow}$ = 1.3]<br>8.7 [experimental log $K_{ow}$ = 0.94] | EPI Suite 2011 |
| | 4.3 [log Kow = 0.63] | | Tomlin 2004 |
| | 1.4 [log Kow = 0.15] | 9.5 [log Kow=0.98] (MRID 435409-03) | U.S. EPA/OPP/EFED 2008a, p. 27; U.S. EPA/OPP/EFED, p. 27 MRID 435409-03 |

| Item | Dazomet | Methyl isothiocyanate | Reference[1] |
|---|---|---|---|
| Molecular weight (g/mole) | 162.27 | 73.11 | EPI Suite 2011a,b |
| Melting point | 106°C | 36°C | ChemIDplus 2013a,b |
| Vapor pressure | 2.8 x $10^{-6}$ mm Hg | 3.54 mm Hg | ChemIDplus 2013a,b |
| | | 19 mm Hg (25°C) | |
| Water solubility | 3000 mg/L | 7600 mg/L | ChemIDplus 2013a,b |
| | | | |
| | **Environmental Properties** | | |
| Bioconcentration in fish (BCF) | 3.162 [estimate] | 3.162 [estimate] | EPI Suite 2011a,b |
| $K_{oc}$ | 83.7 [estimate based on Molecular Connectivity Index]<br>275.4 [estimate based on experimental $K_{ow}$] | 9.3 [experimental Log Koc = 0.97] | EPI Suite 2011a,b |
| Soil/water $K_d$ (L/kg) | | 0.26 | U.S. EPA/OPP/EFED 2008a, p. 28 citing Gerstl et al. 1977 |
| Sediment half-life | 3 hours<br>Major degradate: methyl isothiocyanate and others | | U.S. EPA/OPP/EFED 2008a, MRID 435965-01, p. 27 |
| Soil half-life, aerobic | 17.2 hours [0.71 days]<br>Major degradate: methyl isothiocyanate. | 5.4 and 7 days (loamy sand)<br>20.2 days (sandy loam) | U.S. EPA/OPP/EFED 2008a, MRID 402119-01, p. 27;<br>U.S. EPA/OPP/EFED 2008a, MRID 460847-01, p. 28 |
| | | 3.3 days (for Har Barquan)<br>4.1 days (for Golan)<br>4.6 days (for Belt Nir)<br>5 days (for Gilat and Mivatachim)<br>9.9 days (for Malkiya) | U.S. EPA/OPP/EFED 2008a, p. 28 citing Gerstl et al. 1977 |
| Soil photolysis, $t_{½}$ | 9-10 days<br>Major degradate: methyl isothiocyanate. | | U.S. EPA/OPP/EFED 2008a, MRID 431725-01, p. 26 |
| Field dissipation half-life | 1.5 days (Germany, silt loam soil)<br>1.8 days (Spain, loam sand soil)<br>1.9 days (Spain, loamy sand soil) | | U.S. EPA/OPP/EFED 2008a, MRID 460847-02, p. 27 |
| Field dissipation half-life | | 9.65 days (parent and MITC metabolite in California loamy sand soil) | U.S. EPA/OPP/EFED 2008a, MRID 418748-01 and -02, p. 27 |

[1] When two references are given, the first applies to dazomet and the second applied to methyl isothiocyanate.
[2] There a many sources of information on some standard values – e.g., molecular weight. In general, only two sources as cited for each value. More than two sources are cited only to highlight apparent discrepancies.

See Section 2 for discussion.

**Table 2: Summary of toxicity values used in human health risk assessment**

## Dazomet

| Type of Toxicity Value | Numeric Value | Animal NOAEL | Uncertainty Factor | Reference |
|---|---|---|---|---|
| **Oral** | | | | |
| Acute RfD | 0.03 mg/kg bw/day | 3 mg/kg bw/day (rat, developmental) | 100 | ESFA 2010, p. 7<br>European Union 2012, p. 3 |
| Occupational Limit (AOEL) | 0.015 mg/kg bw/day | 1.5 mg/kg bw/day (rats, 90 day oral study in rats) | 100 | ESFA 2010, p. 7<br>European Union 2012, p. 3 |
| Chronic ADI | 0.01 mg/kg bw/day | 1 mg/kg bw/day (rat, chronic) | 100 | ESFA 2010, p. 7<br>European Union 2012, p. 3 |
| **Dermal** | | | | |
| 1-30 days | 0.15 mg/kg bw/day | Oral LOAEL 15 mg/kg bw/day | 100 MOE | U.S. EPA/OPP/HED 2009a, p. 28 |
| 1-6 Months | 0.015 mg/kg bw/day | Oral NOAEL 1.5 mg/kg bw/day | 100 MOE | U.S. EPA/OPP/HED 2009a, p. 28 |
| Chronic | Not required | | | U.S. EPA/OPP/HED 2009a, p. 28 |

See Section 3.1.1 for discussion

## Methyl Isothiocyanate

| Type of Toxicity Value | Numeric Value | Animal NOAEL | Uncertainty Factor | Reference |
|---|---|---|---|---|
| **Oral** | | | | |
| Acute RfD | 0.03 mg/kg bw | 3 mg/kg bw (rats, developmental study) | 100 | ESFA 2010, p. 7<br>European Union 2012, p. 3 |
| Chronic ADI and AOEL | 0.004 mg/kg bw/day | 0.4 mg/kg bw/day (dog, 90 days) | 100 | ESFA 2010, p. 7<br>European Union 2012, p. 3 |
| **Inhalation** | | | | |
| Acute (1-8 hour) | 0.022 ppm (0.0667 mg/m$^3$ or 66.7 µg/m$^3$) | Based on human eye irritation NOAEL of 0.22 ppm (0.667 mg/m$^3$) and LOAEL of 0.800 ppm (2.426 mg/m$^3$ or 2,426 µg/m3). Exposure period of 1-8 hours. | 10 (for interspecies variability) | U.S. EPA/OPP 2008a, p. 13<br>U.S. EPA/OPP 2008b, p. 18<br>U.S. EPA/OPP/HED 2009a, Table 4.4e, p. 29 |
| Short- and Intermediate-Term Inhalation (1 day to 6 months) | 0.167 mg/m$^3$ or 167 µg/m$^3$ [no effect anticipated]<br>0.33 mg/m$^3$ or 330 µg/m$^3$ [effects possible] | NOAEL: 5 mg/m$^3$ (1.7 ppm, rats, 28-days).<br>LOAEL: 19.9 mg/m$^3$,(6.8 ppm, rats, 28-days) | 30 (MOE) | U.S. EPA/OPP/HED 2009a, Table 4.4e, p. 29. MRID 45314802 |
| RfC (Chronic) | 0.00365 mg/m$^3$ or 3.65 µg/m$^3$ | 30.67 mg/m$^3$ | N.S. | Labat-Anderson 2002, p. 4-12 |

See Section 3.1.2 for discussion

**Table 3: Summary of toxicity values used in ERA**

| Group/Duration | Organism | Endpoint | Toxicity Value (a.i.) | Reference |
|---|---|---|---|---|
| **Terrestrial Animals** | | | | |
| | | **Dazomet** | | |
| **Acute Oral** | | | | |
| | Mammals | Oral $LD_{50}$ | 415 mg/kg bw | Section 4.3.1.1.1 |
| | Birds | Oral $LD_{50}$ | 424 mg/kg bw | Section 4.3.2.1.1 |
| | | **Methyl Isothiocyanate** | | |
| **Acute Oral** | | | | |
| | Mammals | Oral NOAEL | 3 mg/kg bw | Section 4.3.1.1.2 |
| | Birds | No toxicity data | N/A | Section 4.3.1.2.2 |
| **Longer-term Oral** | | | | |
| | Mammals | Oral NOAEL, rats | 0.4 mg/kg bw | Section 4.3.1.1.2 |
| | Birds | No toxicity data | N/A | Section 4.3.1.2.2 |
| **Acute Inhalation** | | | | |
| | Mammals (including canids) | $LC_{50}$ 540 mg/m$^3$ ÷ 10 | 54 mg/m$^3$ | Section 4.3.1.1.2. |
| | Birds | No data | N/A | Section 4.3.1.2.2 |
| **Longer-Term Inhalation** | | | | |
| | Mammals (including canids) | 28-Day Inhalation NOAEL | 5 mg/m$^3$ | Section 4.3.1.1.2. |
| | Bird | No data | N/A | Section 4.3.1.2.2. |
| **Terrestrial Plants** | | **No Data** | | |
| **Aquatic Animals** | | **Methyl Isothiocyanate** | | |
| **Acute** | | | | |
| Fish | Sensitive | Trout $LC_{50}$ 0.094 mg/L ÷ 20 | 0.0047 mg/L | Section 4.3.2.1 |
| | Tolerant | Bluegill $LC_{50}$ 0.142 mg/L ÷ 20 | 0.0071 mg/L | |
| Invertebrates | Sensitive | Not identified. | N/A | Section 4.3.2.2 |
| | Tolerant | Daphnia $LC_{50}$ 0.05 mg/L ÷ 20 | 0.025 | |
| **Longer-term** | | | | |
| Fish | Sensitive | No valid data available | N/A | Section 4.3.2.1 |
| | Tolerant | No valid data available | N/A | |
| Invertebrates | Sensitive | Not identified. | N/A | Section 4.3.2.2 |
| | Tolerant | Daphnia NOAEC | 0.025 mg/L | |
| **Aquatic Plants** | | **Methyl Isothiocyanate** | | |
| Algae | Sensitive | NOAEC, *Scenedesmus subspicatus* | 0.19 mg/L | Section 4.3.2.3.1 |
| | Tolerant | Approximate NOAEC *Anabaena flos-aquae* | 1.1 mg/L [4] | |
| Macrophytes | Sensitive | Not identified | N/A | Section 4.3.2.3.2 |
| | Tolerant | NOAEC, *Lemna gibba* | 0.09 mg/L | |