SERA TR-056-13-02-02b

Mancozeb:
WorksheetMaker Workbook Documentation
Final Report

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July 31, 2015
(August 27, 2015 Minor Correction)

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LIST OF INPUT FILES

Mancozeb WMS Formulation Inputs.docx
Mancozeb WSM Chemical Inputs.docx

Note that the input files are for the SERA 2011b utility. Additional customization of the workbook created by WorksheetMaker is required. See the end of Section 1.2 for details.

REVISION NOTE

Initial
This report is a modification to SERA TR-056-13-02-01a, Mancozeb: WorksheetMaker Workbook Documentation, dated December 20, 2014. Changes to this workbook are based on the following comments from the Forest Service:

Email from John Justin dated July 6, 2015.
Notes from John Justin and Shawna Bautista in an EXCEL workbook (**Mancozeb SAMPLE Workbook-SB-JJ.xlsm**) via an email from Shawna Bautista dated 6/2/2015.
Comments from John Justin in a Microsoft Word file (**Query Template for WSM Input Effort.docx**) via an email from Shawna Bautista dated 12/30/2014.

The most recent comments are given precedence when the feedback is inconsistent or incomplete.

August 27, 2015
On page 22, Line 30 of the final report, 'oryzalin' rather than 'mancozeb' had been incorrectly inserted. This has been corrected.

ACRONYMS, ABBREVIATIONS, AND SYMBOLS

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)
EDBC	ethylenebis-dithiocarbamate
EEC	expected environmental concentration
EFED	Environmental Fate and Effects Division (U.S. EPA/OPP)
ERA	ecological risk assessment
ETU	Ethylenethiourea
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.

While this document and the accompanying EXCEL workbook are intended to be generically useful within the Forest Service, the program/project specific inputs are based on uses at the JH Stone nursery in Central Point, Oregon, with information provided by John Justin (Nursery Manager) and Shawna Bautista (Forest Service Pesticide Use Coordinator). While these program/project specific inputs are used in the current report, all rates, volumes, acres treated, number of applications, and other estimates are estimated based on annual averages. Actual inputs used in a specific application at the JH Stone nursery are determined based on the degree of pest infestation and the acres of the crop to be treated. In assessing an actual application at the JH Stone nursery or other facility or forest, this report and the accompanying WorksheetMaker workbook should be modified using inputs relevant to the specific application.

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1.2. Chemical Specific Information

The current document concerns mancozeb. The initial information on mancozeb was identified at the U.S. EPA's Pesticide Chemical Search website (http://iaspub.epa.gov/apex/pesticides/f?p=CHEMICALSEARCH:1:11098277289067::NO:1::) using the search term "mancozeb". Other information was identified through custom searches of the EPA web site, particularly E-Dockets.

Mancozeb is an ethylene-bis-dithio-carbamate (EBDC) fungicide. U.S. EPA's Pesticide Chemical Search website lists four E-Dockets on mancozeb and 89 cleared science reviews.

TOXLINE (http://toxnet.nlm.nih.gov) contains 2129 open literature citations using synonyms and 1,064 citations not using synonyms. The distinction between using and not using synonyms is important in that using synonyms may lead to irrelevant citations (most often due to formulation names) and not using synonyms may result in missing some relevant citations. As discussed further in Section 2, mancozeb is somewhat unusual in that it is a hydrolytically unstable polymer, and a major metabolite is ethylenethiourea, which is of toxicological concern. The open literature on ethylenethiourea is also substantial with TOXLINE providing 1405 citations with synonyms and 969 citations without synonyms.

Information relating to the human health effects of mancozeb is taken primarily from the human health risk assessment of mancozeb supporting a Section 3 new use (U.S. EPA/OPP/HED 2013a) supplemented by information in the RED for mancozeb (U.S. EPA/OPP 2005a). Information relating to the human health effects of ethylenethiourea is also given in U.S. EPA/OPP/HED (2013a) and is supplemented by an aggregated HHRA for ethylenethiourea as a degradate of mancozeb and other fungicides (U.S. EPA/OPP/HED 2013b). Information on ecological effects and the environmental fate of mancozeb is taken primarily from the EPA's assessment of the potential effects of mancozeb on threatened and endangered species (U.S. EPA/OPP/EFED 2011). General information on mancozeb and ethylenethiourea are taken from Tomlin (2004), EPI Suite (2011), and ChemIDplus (2014).

This document is accompanied by two MS Word files: **`Mancozeb WMS Formulation Inputs.docx`** and **`Mancozeb WSM Chemical Inputs.docx`**. These files can be used with the MS Word utility, SERA (2011b), to add mancozeb to the database used by WorksheetMaker. This document is also accompanied by a WorksheetMaker EXCEL workbook, **`Mancozeb SAMPLE Workbook.xlsm`**. Forest Service personnel may modify this workbook for program specific activities.

Because of several issues associated with the conversion of mancozeb to ethylenethiourea (as discussed in several places in the following sections), several customizations to the WorksheetMaker workbook have been necessary, as listed below:

- Worksheet C01 (general exposure for workers) is modified so that the maximum amount handled by a single worker is 7.875 lbs a.i. The rationale for this approach is detailed in Section 3.2.1.1. **Note that C01 must be modified manually to account for different application rates or amounts.**
- Worksheet E02 (risk characterization for the workers) is modified to use the acute toxicity value for mancozeb (5 mg/kg bw/day) for accidental exposures.
- Worksheet E02 (risk characterization for the workers) is modified to use both acute and chronic toxicity values for both male and female workers for general exposures. Acute toxicity values are used for circumstances in which a compound would be applied only infrequently in a year.
- Worksheet E04 (risk characterization for the general public) is modified so that toxicity values for exposure scenarios associated with the consumption of contaminated vegetation are based on mancozeb (5 mg/kg bw for acute and 0.16 mg/kg bw/day for chronic) and not ethylenethiourea. Note that the chronic exposures for females are based on the population adjusted dose of 0.016 mg/kg bw/day.

- Worksheet E05 for cancer risk is modified to use potency for mancozeb for all scenarios involving the consumption of contaminated vegetation and the potency for ethylenethiourea is used for risks associated with contaminated water. All HQs are based on an incremental risk associated with a 1-day exposure (see Section 3.3.2 for discussion and Section 3.4 for an elaboration of the incremental risk).

2. CHEMICAL/PHYSICAL PROPERTIES

Mancozeb has been registered since 1948 and used in the United States to inhibit damage to crops and ornamentals. Mancozeb as well as maneb and metiram are ethylenebis-dithiocarbamate (EDBC) fungicides. These three EDBC fungicides share a common metabolite, ethylenethiourea (U.S. EPA/OPP 2005a). As discussed further in Section 3, ethylenethiourea is a metabolite of toxicological concern and is classified by the EPA as a probable human carcinogen (U.S. EPA/OPP/HED 2013b).

The U.S. EPA registration review program operates on a 15-year cycle. The reregistration of mancozeb is relatively recent (i.e., U.S. EPA/OPP 2005), however, and the registration review is not scheduled to start until 2015 (U.S. EPA/OPP/2013, p. 21).

As of 2011 (the most recent year for which data are available), the USGS estimates an upper end annual use of mancozeb in the United States of somewhat over 6 million pounds (http://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2011&map=MANCOZEB&hilo=L&disp=Mancozeb). The PAN Pesticides Database currently lists 67 active formulations of mancozeb (Kegley et al. 2014).

The Forest Service specified that the Dithane 75 DF formulation will be used (EPA Registration Number 62719-402). Dithane 75 DF is supplied by Dow AgroSciences and is a 75% a.i. dry flowable formulation. The maximum single application rates for mancozeb considered in the most recent EPA human health risk assessment (i.e., U.S. EPA/OPP/HED 2013a, Table 9.1.1) for applications to tangerines is 1.8 lb a.i./acre. The product label for Dithane 75DF (Dow Label Code D02-179-004) indicates that the maximum single application rate is 17.4 lb a.i./acre and that up to four applications may be made per year with a minimum application interval of 10 days.

The JH Stone Nursery indicated that Dithane 75DF will be used at an application rate of 1.5 lb formulation/acre, which is equivalent to 1.125 lbs a.i./acre [$0.75_{\text{a.i./formulation}}$ x 1.5 lb formulation/acre = 1.125 lb a.i./acre]. Two applications per year with a minimum application interval of 10 days may be made at the nursery to a 7-acre plot. Thus, the total annual use at the nursery is 15.75 lbs a.i. [1.125 lb a.i./acre x 7 acres/application x 2 applications per year], which is equivalent to 7.875 lbs a.i./application.

Based on information from the Forest Service (the illustration in **JH Stone Nursery Information-v3 Shawna Aug 21.docx**), the JH Stone nursery is about 220 acres in size. Using the 7-acre treated area, a proportion of about 0.032 [7 acres ÷ 220 acres ≈ 0.031818…] of the nursery area would be treated. As discussed further in Section 3.2.2.1, this proportion is used to modify the water contamination rates.

Another important formulation specific input for WorksheetMaker is the application volume—i.e., the gallons/acre applied of the field solution after mixing. The application volume to be used at the JH Stone nursery is specified as 30 gallons/acre by broadcast spray using tractor mounted spray booms. While application volumes may be entered as a central estimate with upper and lower bounds, the WorksheetMaker workbook that accompanies this analysis is based only on 30 gallons per acre in Worksheet A01.

Table 1 summarizes the chemical and physical properties of mancozeb. Mancozeb is unusual in that it is an unstable polymer that breaks down relatively rapidly in the environment. A brief synopsis of the complexity that these characteristics add to a risk assessment is given below from the most recent U.S. EPA/OPP ecological risk assessment:

> *The chemical* [mancozeb] *is a polymer or highly coordinated salt complex, in which the EBDC* [ethylene-bis-dithio-carbamate] *ligand is present in coordination with zinc (ZN+2) and manganese (Mn+2) ions. The parent mancozeb is expected to be hydrolytically unstable in the natural environment as it is applied under moist conditions. Therefore, this risk assessment is based on estimates of exposure to the mancozeb hydrolytic residue; referred to hereafter as the mancozeb complex. As discussed later, the mancozeb complex consists of multi-chemical species including the major degradate ethylenethiourea (ETU). In the risk assessment process, both acute and chronic exposure concentrations will be estimated for the total toxic residue or mancozeb complex. It is noted, however that the chemical species present in the "fresh" mancozeb complex at the short-term, which are believed to be those chemical species responsible for observed acute toxicity of mancozeb, include ETU. In contrast, the "aged: mancozeb complex is expected to be enriched with ETU. Use of the total toxic residue procedure in the risk assessment process was necessary due to the unique hydrolytic instability of mancozeb and the formation of mancozeb complex.*
>
> U.S. EPA/OPP/EFED (2011, p. 11)

Essentially, the approach used in U.S. EPA/OPP/EFED (2011) adopts the 'mixture of concern' approach in the EPA's mixture risk assessment guidance (U.S. EPA/ORD 2000, Section 2.5.1, p. 23) with the qualification that the complex mixture may change over time with increasing amounts of ethylenethiourea in the mixture as the mixture weathers. This position appears to be reasonable, particularly for aquatic species, in that ethylenethiourea is less toxic than mancozeb by 2 to 3 orders of magnitude (U.S. EPA/OPP/EFED 2011, p. 30)

While focus on the total toxic residues as the agent of concern may be reasonable for the ecological risk assessment, matters are further complicated in that Health Effects Division of the U.S. EPA/OPP determined that ethylenethiourea is the only agent of concern in drinking water exposures (U.S. EPA/OPP/HED 2013a, p. 4).

As discussed further in the exposure assessments—i.e., Section 3.2 for human health and Section 4.2 for ecological effects—and noted at the end of Section 1.2, these unusual conditions relating to the formation of ethylenethiourea and the complexity of mancozeb residues require customization of the WorksheetMaker workbook.

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. U.S. EPA/OPP/HED (2013a) provides an extensive discussion of the toxicology of mancozeb and ethylenethiourea, and additional information on ethylenethiourea is presented in U.S. EPA/OPP/HED (2013b). As discussed below, the thyroid is the primary target tissue for both mancozeb and ethylenethiourea. As noted in U.S. EPA/OPP/HED (2013a, p. 5): *The database for mancozeb is extensive and is sufficient for characterizing toxicity and hazard*. The lack of a developmental thyroid toxicity study in rats is the only significant data gap for mancozeb identified by EPA. The U.S. EPA/OPP/HED (2013a, p. 9) identifies the following data gaps on ethylenethiourea: … *a 2-generation reproduction study in rats, a developmental neurotoxicity study in rats, and a developmental thyroid toxicity study in rats*. These data gaps are being addressed by ongoing studies.

The toxicity of mancozeb and ethylenethiourea are similar. Neither mancozeb nor ethylenethiourea is classified as highly toxic on an acute basis. Mancozeb is classified as Category IV for acute oral, dermal, and inhalation toxicity as well as skin irritation. Mancozeb is does not cause skin irritation and is only a mild eye irritant (Category III) (U.S. EPA/OPP/HED 2013a, p. 70). Similarly, ethylenethiourea is classified as only moderately toxic on dermal exposure (Category III) and relatively nontoxic in terms of acute inhalation exposure, eye irritation, and skin irritation (Category IV). No data appear to be available on the acute oral toxicity or dermal sensitization potential of ethylenethiourea (U.S. EPA/OPP/HED 2013a, p. 72).

The longer-term toxicity of mancozeb to mammals appears to be largely associated with the metabolism of mancozeb to ethylenethiourea. Ethylenethiourea is a major metabolite of mancozeb in rats. The primary target organ for both mancozeb and ethylenethiourea is the thyroid. Mancozeb causes changes in thyroid hormone levels, increased thyroid weight, and damage to thyroid tissue. The effects of mancozeb on the thyroid appear to be attributable to the formation of ethylenethiourea and the inhibition of thyroid peroxidase. As discussed further in Section 3.3, both mancozeb and ethylenethiourea are classified as carcinogens, and the potential cancer risk associated with exposures to mancozeb is quantified based on the cancer potency of ethylenethiourea (U.S. EPA/OPP/HED 2013a).

3.2. Exposure Assessment

3.2.1. Workers

3.2.1.1. General Exposures

As discussed in SERA (2014b), Forest Service risk assessments use a standard set of worker exposure rates (Table 14 in SERA 2014b). The application of these standard methods to mancozeb is complicated by co-exposure to mancozeb and ethylenethiourea, which will occur during applications.

As a simplification, the current assessment focuses on worker exposures to ethylenethiourea. This approach is based on the worker exposure assessments given in U.S. EPA/OPP/HED

(2013a, Section 9.1, pp. 55-64) for both mancozeb and ethylenethiourea. As summarized in these EPA exposure assessments, aerial applications may be a concern in terms of exposures to both mancozeb and ethylenethiourea. Aerial applications, however, are not relevant to the JH Stone nursery.

For non-aerial applications, exposures based on mancozeb lead to MOEs in the range of 5000 to over 300,000. Given the EPA's designated levels of concern for female workers (i.e., 30 as designated in Table 9.1.1), these MOEs corresponds to HQs in the range of about 0.00009 [1÷ (343,100÷30)] to 0.006 [1÷ (5000÷30)]. In other words, the exposures to mancozeb itself are far below the level of concern. Exposure assessments for ethylenethiourea based on both direct exposure and exposure to ethylenethiourea from the metabolism of mancozeb, (Table 9.1.2 in U.S. EPA/OPP/HED 2013a) lead to lower MOEs (i.e., higher risk) for non-aerial applications—i.e., 2000 with a MOE of 30, which corresponds to an HQ of 0.015 [1÷(2000÷30)].

As specified in Table 9.1.2 of the EPA exposure assessment, the total dose of ethylenethiourea associated with the MOE of 2000 is estimated as 0.002486 mg/kg bw. This dose, in turn, is based on the treatment of 40 acres at an application rate of 1.8 lb a.i./acre, which is equivalent to handling 72 lbs of mancozeb. Thus, the implicit exposure rate in the EPA exposure assessment is 0.0000345 mg/kg bw/day per lb a.i. handled [0.002486 mg/kg bw/day ÷ 72 lbs. handled] where the dose refers to ethylenethiourea and the amount handled refers to mancozeb. This may be viewed as a conservative exposure assessment in that the exposure is based on open cab ground broadcast applications.

The exposure rates for ground broadcast applications used in Forest Service risk assessments (central estimate and 95% prediction interval) are 0.0001 (0.000002 to 0.005) mg/kg bw per lb a.i. handled (SERA 2014b, Table 14). The central estimate is greater than the EPA estimate by a factor of about 3 [0.0001 ÷ 0.0000345 ≈ 2.89]. This comparison, however, is flawed in that the standard Forest Service rate is based on exposure to the compound applied. As discussed in the EPA risk assessment, a correction factor of 7.5% is applied to the mancozeb exposure level to estimate the conversion of mancozeb to ethylenethiourea (U.S. EPA/OPP/HED 2013a, p. 4). Applying this correction factor, the adjusted rates from SERA (2014b) are 0.0000075 (0.00000015 to 0.000375) mg/kg bw/day per lb a.i. handled. With this adjustment, the central estimate of the SERA rate is a factor of about 5 below the EPA rate [0.0000345 ÷ 0.0000075 ≈ 4.6037]; however, the upper bound of the SERA estimate is higher than the EPA rate by about a factor of 11 [0.000375 ÷ 0.0000345 ≈ 10.86082]. In the WorksheetMaker workbook that accompanies this document, the adjusted SERA rates of 0.0000075 (0.00000015 to 0.000375) mg/kg bw/day per lb a.i. handled and risks associated with these exposure rates are assessed using the acute RfD for ethylenethiourea (Section 3.3). As detailed in Section 3.3, an added complication involves the potentially increased sensitivity of female workers to ethylenethiourea.

As summarized in SERA (2014a, Table 6), standard assumptions for broadcast foliar applications in Forest Service risk assessments assume that workers will treat 112 (66 to 168) acres/day. The JH Stone Nursery, however, specified that workers will treat at a rate of 4 to 5 acres per hour over a 2- to 3-hour period. At an application rate of 1.125 lbs a.i./acre, these rates are equivalent to 9 lbs a.i./day [4 acres/hour x 2 hours/day x 1.125 lbs a.i./acre] to 16.875 lbs a.i./acre [5 acres/hour x 3 hours/day x 1.125 lbs a.i./acre]. As discussed in Section 2, however, the JH Stone Nursery indicated that only 7 acres/day will be treated at a rate of 1.125 lb a.i./acre, which is equivalent to 7.875 lbs a.i. Thus, Worksheet C01 is customized to set the amount handled by a worker per day to 7.875 lbs a.i.

3.2.1.2. Accidental Exposures

In addition to general exposures, four standard accidental exposure scenarios for workers discussed in SERA (2014a, Section 3.2.2.2) are also considered, and they are detailed in Worksheets C02a,b and C03a,b. Because these accidental scenarios involve short-term exposures which occur during application, mancozeb rather than ethylenethiourea is the agent of concern.

3.2.1.2.1. Spills

Worksheets C03a,b involve accidental spills under the assumption of first-order dermal absorption. These scenarios require an estimate of the first-order dermal absorption rate coefficient (k_a). Based on two dermal absorption studies, the U.S. EPA/OPP/HED (2013a) uses a dermal absorption factor of 1%. This factor is used for exposures over the course of a work day (8 hours) and corresponds to an estimated first-order dermal absorption rate of 0.00126 $hour^{-1}$ [$k_a = -\ln(1\text{-}0.01)\div 8 \text{ hours} \approx 0.00126 \text{ hour}^{-1}$].

In the absence of experimental data, Forest Service risk assessments use an algorithm based on the molecular weight and octanol water partition coefficient (K_{ow}) to approximate a first-order dermal absorption rate coefficient—i.e., Eq. 23, Section 3.1.3.2.2 in SERA 2014a. As detailed in Worksheet B03b of the WorksheetMaker workbook that accompanies this report, the estimated first-order dermal absorption rate coefficient for mancozeb based on this algorithm is 0.0012 (0.00051 to 0.003) $hour^{-1}$ based on a molecular weight of 271.2 and K_{ow} of 3.24 (Table 1 values from U.S. EPA/OPP/HED 2013). The central estimate of the k_a (0.0012 $hour^{-1}$) from the SERA (2014a) algorithm is virtually identical to the estimate of 0.00126 $hour^{-1}$ from U.S. EPA/OPP/HED (2013a). This concordance is somewhat unexpected and may be fortuitous. As discussed in Section 2, mancozeb is a complex mixture and the molecular of 271.2 g/mole essential applies to the monomer. Nonetheless, given the concordance of the two estimates, the current assessment uses the k_a values of 0.0012 (0.00051 to 0.003) $hour^{-1}$ from the SERA (2014a) algorithm to more explicitly account for the uncertainty of the estimate.

3.2.1.2.2. Contaminated Gloves

Worksheets C02a,b involve contaminated gloves under the assumption of zero-order dermal absorption. These scenarios require an estimate of the skin permeability coefficient (K_p in units of cm/hr). No experimental measurements of K_p were identified in the literature reviewed for this report (Section 1.2). Consequently, the K_p is estimated using an algorithm developed by the U.S. EPA's Office of Research and Development as discussed in SERA (2014a, 3.1.3.2.1). The application of this algorithm to mancozeb is detailed in Worksheet B03a of the WorksheetMaker workbook that accompanies this document. These values are rounded to 0.000093 (0.000051 to 0.00017) cm/hr in Worksheets C02a,b.

3.2.2. General Public

As detailed in SERA (2014a, Section 3.2.3), Forest Service risk assessments provide a standard set of exposure scenarios for members of the general public. These exposure scenarios are applicable to standard forestry applications of pesticides and are included in the WorksheetMaker workbook that accompanies this document.

3.2.2.1. Surface Water

Full Forest Service risk assessments typically estimate concentrations of a pesticide in surface water using GLEAMS-Driver (SERA 2014a, Section 3.2.3.4.3). In the interest of economy, the current analysis uses FIRST (FQPA Index Reservoir Screening Tool). FIRST is a Tier 1 model developed by the U.S. EPA to estimate pesticide concentrations in surface water, and details of the FIRST model are available at http://www.epa.gov/oppefed1/models/water/first_description.htm.

The surface water estimates for the current assessment are somewhat complicated by the need to consider ethylenethiourea as well as mancozeb. Following the approach taken in U.S. EPA/OPP/HED (2013a), ethylenethiourea is considered the only agent of concern. As discussed further in Section 4.2.3, the ecological risk assessment is based on mancozeb.

The input parameters for the FIRST model and the estimated concentrations of ethylenethiourea in surface water are summarized in Table 2. The output files from FIRST for these simulations are given in Appendix 1. As with standard GLEAMS-Driver modeling, a unit application rate of 1 lb a.i./acre is used. Note that the application is in terms of mancozeb. Following the general approach used in U.S. EPA/OPP/HED (2013a, p. 4), a correction factor of 7.5% is applied to the mancozeb exposure level to estimate the conversion of mancozeb to ethylenethiourea. Thus, the application rate actually entered into the FIRST model is 0.075 lb ethylenethiourea/acre.

One very important input parameter for FIRST is the proportion of the watershed that is treated. As indicated in Table 2, the FIRST modeling was conducted using a proportion of 1.0—i.e., the entire watershed is treated. The concentrations given in Table 2 can be adjusted downward if only a fraction of the area under consideration (i.e., the relevant watershed) is treated.

The current analysis is focused on the JH Stone Nursery. As discussed in Section 2, the current analysis anticipates that about 0.032 of the nursery's fields would be treated with mancozeb. As also illustrated in Table 2, this proportion is used to reduce the surface water concentrations anticipated at the JH Stone nursery. Since the watershed in the vicinity of the JH Stone nursery is larger than the area of the nursery itself, this approach is conservative in that the concentrations of ethylenethiourea in surface water are probably grossly over-estimated.

The above approach to surface water modeling is simplistic, relative to the processes involving the conversion of mancozeb to ethylenethiourea. U.S. EPA/OPP/HED (2013a, Section 5.3, pp. 30-31) uses a more sophisticated modeling approach (PRZM/EXAMS) to estimate total concentrations of ethylenethiourea in surface water from the use of mancozeb from all EDBC pesticides. For comparison, U.S. EPA/OPP/HED (2013a, Table 5.3, p. 31) estimates surface water concentrations of 0.1 to 25.2 µg/L for peak exposures and 0.1 µg/L for longer-term exposures. As indicated in Table 2 of the current document, the estimates for the JH Stone nursery are peak concentrations of 0.086 (0.076-0.101) µg/L and longer-term concentrations of 0.031 (0.004 to 0.022) µg/L. An issue with the FIRST analysis is that the longer-term upper bound concentration (0.679 µg/L) is below the corresponding central estimate (0.0679 µg/L). This does not appear to be an input error and appears to relate to impact of K_{oc} on longer-term concentrations.

An alternative approach to estimating the contamination of surface water may be based on the PRZM/EXAMS modeling in U.S. EPA/OPP/EFED (2011). As summarized in Section 2, EFED elected to model total toxic concentration of both mancozeb and ethylenethiourea in surface water. The inputs for this modeling (U.S. EPA/OPP/EFED 2011, Table 3-2), however, are very similar to the inputs used in the application of FIRST, as discussed above.

A summary of the EFED modeling is given in Table 3. The application rates and number of applications in Table 3 of the current report are taken from U.S. EPA/OPP/EFED 2011, Table 3-1. The EECs are taken from Table 3-3 of the EFED report. The total cumulative application rate is taken as the product of the maximum application rate and number of applications. Note that EFED gives the application rates in units of kg/ha. The total cumulative application rate is converted to lb/acre [1 lb/acre = 0.892 kg/ha]. The peak and longer-term Water Contamination Rates (WCRs) are calculated as the corresponding concentrations divided by the cumulative application rate in lb/acre. The lower section of Table 3 gives the mean, 5% lower bound, and 95% upper bound of the WCRs—i.e., mean and 90% confidence interval. The calculations of the confidence intervals are given in Appendix 2 (peak concentrations) and Appendix 3 (longer-term concentrations).

The average of the peak and longer-term WCRs from the EFED modeling (2.29 and 0.422 µg/L) are similar to the corresponding values based on the FIRST modelling (2.68 and 0.984 µg/L as summarized in Table 2 of the current report). In addition, the upper bounds of peak and longer-term WCRs from the EFED modeling (2.84 and 0.514µg/L) are similar to the corresponding upper bounds from the FIRST modelling (3.169 and 0.679 µg/L). The EFED modeling is detailed, well documented, and consistent with the estimates from U.S. EPA/OPP/HED (2013a). Thus, the peak and longer-term WCR values from EFED (Table 3 of the current document) are used with the factor of 0.032 (i.e., the proportion of the nursery's fields that would be treated) to estimate concentrations of mancozeb total toxic residues in surface water. These calculations are detailed in Table 4. The results from the modeling summarized in Table 4 are entered into Worksheet B04Rt as water contamination rates—i.e., mg/L per lb a.i./acre applied.

In the interest of transparency, it is emphasized that the surface water concentrations in Table 4 are used in both the human health and ecological risk assessments. This may appear to be conceptually inconsistent with U.S. EPA/OPP/HED (2013a) which focuses on only ethylenethiourea in surface water. As discussed above, however, the concentration estimates from U.S. EPA/OPP/HED (2013a) do not appear to differ substantially from the estimates in U.S. EPA/OPP/EFED (2011). In a more robust analysis, GLEAMS-Driver probably would be run multiple times to more explicitly differentiate concentrations of mancozeb total residues and ethylenethiourea in surface water.

3.2.2.2. Vegetation

As detailed in SERA (2014a, Section 3.2.3.7), several scenarios involving the consumption of contaminated vegetation are included in workbooks produced by WorksheetMaker for pesticides applied to foliage. The major input parameters are application rate, number of applications, and application interval.

For longer-term exposures, half-lives on vegetation are also important parameters. As summarized in Table 1, Knisel and Davis (2000) report a foliar half-life of 10 days for mancozeb. The U.S. EPA/OPP/EFED (2011, p. 64) estimates a foliar half-life of 20 days based …*the 90th percentile of foliar residue data*. In the absence of data, U.S. EPA/OPP typically uses a half-life of 35 days adopted from Willis and McDowell (1987). For the current analysis, a range of 10 to 35 days is used with a central estimate of 20 days—i.e., the approximate geometric mean of the range of 10 to 35 days.

The U.S. EPA/OPP/HED (2013a, Table 5.4.6.1, pp. 33-34) estimates dietary exposures only for mancozeb. The same approach is adopted in this analysis. Consequently, as discussed further in Section 3.4.2, all dietary exposures are expressed using toxicity values for mancozeb.

3.2.2.3. Bioconcentration

As discussed in SERA (2014a, Section 3.2.3.5), scenarios involving the consumption of contaminated fish are included in most WorksheetMaker workbooks. The major chemical specific inputs are the concentrations in surface water (discussed in Section 3.2.1.1 of this document) and the bioconcentration factor (BCF). For exposure scenarios involving humans, the BCF is based on the edible portion (muscle) in fish. For the ecological risk assessment, the BCF is based on whole fish. When adequate data are available, separate BCF values may be given for acute exposures and longer-term exposures.

As with other exposure scenarios involving contaminated surface water, the agent of concern is ethylenethiourea. As summarized in Table 1, the only information on the bioconcentration of ethylenethiourea is an estimate of 3.162 L/kg from EPI Suite (2011). In the absence of additional information, this bioconcentration factor is used in all exposure scenarios involving the consumption of contaminated fish.

3.2.2.4. Dermal Exposure

Several dermal exposure scenarios involving members of the general public are given in WorksheetMaker workbooks. Details of these exposure scenarios are given in SERA (2014a, Sections 3.2.3.3 and 3.2.3.6). The dermal absorption values used in these scenarios are identical to those used for workers. The estimates of dermal absorption rates for these scenarios are identical to those used in the accidental dermal exposure assessments for workers (Section 3.2.1.2 of the current document).

3.3. Dose-Response Assessment

The dose-response assessments for mancozeb are summarized in Table 5, and the dose-response assessments for ethylenethiourea are summarized in Table 6. All of the toxicity values are taken from U.S. EPA/OPP/HED (2013a). The cancer potency factor is taken from U.S. EPA/OPP/HED (2013a) but modified to reflect an incremental risk associated with a single day of exposure, as discussed below (Section 3.3.2).

3.3.1. Systemic Toxicity

As with several aspects of the exposure assessments (Section 3.2), the dose-response assessment is complicated by the consideration of both mancozeb and ethylenethiourea. Toxicity values for mancozeb are used for acute exposures in workers as well as acute and longer-term exposures for the consumption of contaminated vegetation. Longer-term toxicity values for ethylenethiourea are used for non-accidental occupational exposures. As discussed in Section 3.2.1.1, this approach is a simplification of the approach used in U.S. EPA/OPP/HED (2013a) and is based on the EPA finding that the greatest risks in occupational exposures are associated with ethylenethiourea, rather than mancozeb. As with the approach taken by U.S. EPA/OPP/HED (2013a), a more refined analysis would involve separate assessments of occupational exposures to both mancozeb and ethylenethiourea.

An added complication in the dose-response assessment for both mancozeb and ethylenethiourea involves special concern for women of child-bearing age. This concern relates to the ability of both mancozeb and ethylenethiourea to cause malformations in rats in standard developmental studies (U.S. EPA/OPP/HED 2013a, p. 16).

Following the approach used in U.S. EPA/OPP/HED (2013a), all exposures to members of the general public involving contaminated surface water are based on ethylenethiourea rather than mancozeb.

3.3.2. Carcinogenicity

A final complication to the dose-response assessments involves potential carcinogenicity.

The EPA derived a lifetime cancer potency factor of 0.0601 $(mg/kg\ bw/day)^{-1}$ for ethylenethiourea (U.S. EPA/OPP/HED 2013a, p. 5). A cancer potency factor for mancozeb has not been explicitly derived from cancer bioassays on mancozeb. Instead, risks of cancer associated with exposures to mancozeb are estimated by multiplying the cancer potency factor for ethylenethiourea by the conversion factor of 0.075 for the conversion of mancozeb to ethylenethiourea (U.S. EPA/OPP/HED 2013a, p. 23). Thus, the lifetime cancer potency factor of mancozeb is estimated as 0.0045 $(mg/kg\ bw/day)^{-1}$ [0.0601 $(mg/kg\ bw/day)^{-1}$ x 0.075 = 0.0045075 $(mg/kg\ bw/day)^{-1}$].

Following standard practice for WorksheetMaker workbooks, the potency factors are not used directly. Instead, the toxicity values for carcinogenicity are based on a dose associated with a risk of 1-in-1 million. Risk is simply the product of potency and dose [Risk = Potency x Dose]. By rearrangement, the dose associated with a risk of 1-in-1 million (0.000001) is calculated as 0.000001 divided by the potency. Thus, the doses associated with a risk of 1-in-1 million are 0.000017 mg/kg bw/day for ethylenethiourea [0.000001 ÷ 0.0601 $(mg/kg\ bw/day)^{-1} \approx 1.66389 \times 10^{-5}$] and 0.00022 mg/kg bw/day for mancozeb [0.000001 ÷ 0.0045 $(mg/kg\ bw/day)^{-1} \approx$

0.0002222…]. Note that these potency factors and doses for a risk of 1-in-1-million are associated with lifetime exposures.

For the analysis relating to the JH Stone Nursery, lifetime exposures are not anticipated. For less-than-lifetime exposures, the U.S. EPA recommends estimating a dose based on an equivalent lifetime exposure:

> *Unless there is evidence to the contrary in a particular case, the cumulative dose received over a lifetime, expressed as average daily exposure prorated over a lifetime, is recommended as an appropriate measure of exposure to a carcinogen. That is, the assumption is made that a high dose of a carcinogen received over a short period of time is equivalent to a corresponding low dose spread over a lifetime.*
>
> U.S. EPA/RAF (2005, p. 3-26.)

The above approach is essentially identical to the application of Haber's Law as discussed in SERA (2014a, p. 145).

Taking 70 years as a standard value for a human lifetime, the number of days of exposure for a lifetime dose would be 25,000 day [70 years x 365.25 day = 25,567.5 days]. For ethylenethiourea, a daily dose of 0.000017 mg/kg bw/day over a lifetime would be equivalent to a single dose of 0.425 mg/kg bw [0.000017 mg/kg bw/day x 25,000 days = 0.425 mg/kg bw]. For mancozeb, a daily dose of 0.00022 mg/kg bw/day over a lifetime would be equivalent to a single dose of 5.5 mg/kg bw [0.00022 mg/kg bw/day x 25,000 days = 5.5 mg/kg bw]. These doses may be viewed as the dose associated with a 1-day exposure resulting in a lifetime risk of 1-in-1 million. This risk is incremental. For example, an exposure of a period of 10 days would be associated with a risk of 1-in-100,000. A further elaboration of incremental risk is given in Section 3.4.

WorksheetMaker does not accommodate different cancer potency factors for different exposure scenarios. Thus, Worksheet E05 of the workbook accompanying this report is customized to use the cancer potency factor for ethylenethiourea for risks associated with the consumption of contaminated water because the estimates of water exposure are adjusted to represent ethylenethiourea (Section 3.2.2.1). For the consumption of contaminated vegetation, the potency factor for mancozeb is used because the exposure assessments for the consumption of contaminated vegetation are based on residues of mancozeb (Section 3.2.2.2).

3.4. Risk Characterization

3.4.1. Workers

The HQs for workers associated with systemic toxic effects are summarized in Worksheet E02. None of the acute HQs (accidental and general exposures) exceed a level of concern. Given the limited use of mancozeb at the JH Stone nursery, these are probably the most relevant HQs. Nonetheless, it should be noted that the acute HQs for women are 0.005 (0.00009 to 0.2) and are substantially higher than the acute HQs for men—i.e., 0.00001 (0.0000002 to 0.0006). These differences follow from the different acute RfDs for mancozeb derived by the EPA for men and women, as detailed in Table 5.

As discussed in Section 3.3.1, the longer-term HQs for workers are based on ethylenethiourea following the approach used in U.S. EPA/OPP/HED (2013a). As with mancozeb, different longer-term RfDs for ethylenethiourea are derived for men (0.0018 mg/kg bw/day) and women (0.00018 mg/kg bw/day), as detailed in Table 6. The upper bound of the longer-term HQ for male workers is 1.6, modestly exceeding the level of concern (HQ=1). The upper bound of the longer term HQ for female workers is 16, which substantially exceeds the level of concern.

Based on a 1-day incremental cancer risk (Section 3.3.2), none of the HQs for workers approaches a level of concern. The upper bound HQ is about 0.0069. In other words, a worker would need to apply mancozeb for about 144 days to reach the level of concern for a cancer risk of 1-in-1-million.

3.4.2. General Public

The HQs for members of the general public associated with systemic toxic effects are summarized in Worksheet E04. None of the acute non-accidental exposure scenarios exceed the level of concern. Some of the accidental exposure scenarios involving an accidental spill do exceed the level of concern. The highest HQs are associated with the consumption of contaminated water by a child—i.e., HQs of 3 (0.3 to 8). In the event of an accidental spill, vigorous measures to limit exposure of members of the general public would be warranted.

Longer-term exposures associated with the consumption of contaminated water do not exceed the level of concern. Exposures associated with the consumption of contaminated vegetation, however, do exceed the level of concern. The highest HQs are associated with the consumption of contaminated vegetation by a woman—i.e., HQs of 3 (0.1 to 44). The relevance of these HQs to a nursery environment is questionable. Nonetheless, measures may be justified to ensure that the general public will not consume treated vegetation from the nursery.

As summarized in Worksheet E05, none of the HQs associated with an incremental risk of an exposure for 1 day exceeds the level of concern. The upper bound HQ for the consumption of contaminated vegetation, however, is 0.1. Thus, an exposure for 10 days would reach a level of concern for a risk of 1-in-1-million. As with the HQs for systemic toxicity, measures to ensure that the general public will not consume treated vegetation from the nursery are justified.

4. ECOLOGICAL EFFECTS

4.1. Hazard Identification

As with human health effects (Section 3.1), a hazard identification is not developed in the current document in the interest of economy. The most recent EPA ecological risk assessment (U.S. EPA/OPP/EFED 2011) provides an extensive discussion of the toxicity of mancozeb and ethylenethiourea to ecological receptors. Also as with the human health risk assessment, the ecological risk assessment is complicated by considerations of the formation and toxicity of ethylenethiourea.

4.2. Exposure Assessment

4.2.1. Bioconcentration

Typically, bioconcentration values for whole fish are used in the ecological risk assessment, and bioconcentration factors for the edible portion of fish (i.e., muscle) are used in the human health risk assessment. As discussed in Section 3.2.2.3, however, very little information is available on the bioconcentration of ethylenethiourea—i.e., a single estimate of 3.162 L/kg from EPI Suite (2011). This bioconcentration factor is used in both exposure scenarios for wildlife and humans.

4.2.2. Offsite Contamination of Soil

Rates for the offsite contamination of soil are typically handled in full or scoping level Forest Service risk assessments using GLEAMS-Driver modelling. In the interest of economy, the current effort uses a central estimate of 5% with a range of 1% to 10% of the nominal application rate). These values are similar to estimates of offsite losses noted in Forest Service pesticide risk assessments as well as assumptions often used in EPA risk assessments.

4.2.3. Surface Water

As with most full Forest Service risk assessments, the surface water concentrations used in the ecological risk assessment are identical to those used in the human health risk assessment. As discussed in Section 3.2.1.1, the surface water concentrations are based on the PRZM/EXAMS modeling (Tier II) from the most recent EPA ecological risk assessment (U.S. EPA/OPP/EFED 2011) rather than the Tier I FIRST model. As noted in Section 2, the modeling used in the EPA ecological risk assessment is intended to encompass *the mancozeb complex* —i.e., mancozeb and toxic degradation products including ethylenethiourea.

4.3. Dose-Response Assessment

The dose response assessment for nontarget organisms is summarized in Table 7 and is discussed in the following subsections on different groups of receptors.

The dose-response assessments for the receptors covered in this ecological risk assessment are based on the dose-response assessments from the most recent U.S. EPA ecological risk assessment (U.S. EPA/OPP/EFED 2011). In the interest of brevity, this risk assessment is sometimes designated as 'the EFED assessment' or a similar term when this designation appears to be unambiguous. In addition, Appendix D from U.S. EPA/OPP/EFED (2011) is a more detailed summary of the available studies, and this appendix is sometimes referred to as 'Appendix D of the EFED assessment' when there appears to be little potential for ambiguity.

As noted in the EFED risk assessment, *the most sensitive avian and mammalian toxicity endpoints for either mancozeb or ETU were used* (U.S. EPA/OPP/EFED 2011, p. 65). The EPA risk assessment takes essentially the same approach for aquatic organisms:

> *In considering the available data, the most sensitive toxicity endpoints for either mancozeb or ETU were selected for two reasons: (1) the EECs reflect a mancozeb complex (which includes some ETU for short term and much ETU in the long-term), and (2) it is unclear under laboratory toxicity test conditions how much parent mancozeb would be converted to ETU under acute and chronic exposures. Therefore, selecting the most sensitive of the two endpoints (when both were available) reflects a conservative approach for addressing this uncertainty in the effects assessment.*
>
> U.S. EPA/OPP/EFED (2011, p. 68)

The current assessment adopts the same approach used by EPA: When data are available on both mancozeb and ethylenethiourea for a specific receptor, the lower toxicity value is used. Otherwise, the toxicity value for either mancozeb or ethylenethiourea is used if a suitable toxicity value is available on only one of the compounds for the receptor of concern.

Admittedly, this approach does not explicitly consider the joint exposures to mancozeb and ethylenethiourea. Nonetheless, the approach used in U.S. EPA/OPP/EFED (2011) is clearly justified given the very complex nature of the degradation of and changes in the mancozeb complex over time.

With the exception of mammals (as discussed in Section 4.3.1.1), Forest Service risk assessments generally defer to dose-response assessments from U.S. EPA/OPP/EFED in the selection of endpoints and study selection in the dose-response assessments for ecological receptors unless there is a compelling reason to do otherwise. For endpoints associated with acute toxicity, however, the Forest Service prefers to use NOAECs rather than estimates of 50% lethality (LD_{50} or LC_{50} values) which are used in EPA risk assessments. In the absence of an NOAEC, Forest Service risk assessments use LD_{50} or LC_{50} values to approximate an NOAEC by dividing the lethality value by a factor of 10 for terrestrial species or 20 for aquatic species. This approach is based on and is consistent with the EPA variable level of concern approach as detailed in SERA (2014, Section 4.3.2, Table 19). References to the use of this procedure are noted below as appropriate.

4.3.1. Terrestrial Organisms

4.3.1.1. Mammals

4.3.1.1.1. Acute Toxicity

To characterize risk to mammals associated with acute exposures to pesticides, Forest Service risk assessments typically use the acute NOAEL from the human health risk assessment that forms the basis of the acute RfD. As discussed in Section 3.3, the acute NOAEL is 500 mg/kg bw/day for mancozeb (Table 5) and 5 mg/kg bw for ethylenethiourea (Table 6). In the human health risk assessment, acute exposures are based on the toxicity of mancozeb. Thus, for the ecological risk assessment, the NOAEL of 500 mg/kg bw is used.

4.3.1.1.2. Chronic Toxicity

The chronic NOAEL for mancozeb used in the human health risk assessment is 4.83 mg/kg bw/day (Table 5), and the corresponding value for ethylenethiourea is 0.18 mg/kg bw/day (Table 6). Again, for the same reason noted in the selection of acute NOAEL, the lower NOAEL of 0.18 mg/kg bw/day is used for risk characterization of longer-term exposures of mammalian wildlife to the mancozeb complex.

4.3.1.2. Birds

4.3.1.2.1. Acute Toxicity

U.S. EPA/OPP/EFED (2011, Table 5-8, p. 97) does not derive a quantitative risk characterization for acute exposures of birds *…due to no definitive endpoints available*. The EPA document, however, notes an approximate LD_{50} of 1500 mg/kg bw for the English sparrow and characterizes this species as the most sensitive species (U.S. EPA/OPP/EFED 2011, p. 74). A somewhat more detailed tabular summary of toxicity studies in birds (U.S. EPA/OPP/EFED 2011, Appendix D, pp. 6-7) confirms this information. Data on the acute toxicity of ethylenethiourea is not discussed in the EFED risk assessment.

For the current analysis, the LD_{50} of 1500 mg/kg bw is divided by a factor of 10 to approximate a NOAEC of 150 mg/kg bw based on the toxicity of mancozeb.

4.3.1.2.2. Longer-Term Toxicity

To characterize risks to birds associated with longer-term exposures to mancozeb, U.S. EPA/OPP/EFED (2011, Table 4-4, p. 73) uses a NOAEL of 125 mg/kg bw chow from a reproductive study in mallard ducks (MRID 41948401). Using a food consumption rate of 0.07 chow/kg bw for longer-term studies in quail and mallards (SERA 2007a), the dietary NOAEL of 125 mg/kg chow corresponds to dose of 8.75 mg/kg bw/day [125 mg/kg chow x 0.07 chow/kg bw/day ≈ 8.75 mg /kg bw]. Thus, for the current analysis, the NOAEC of 8.75 mg/kg bw/day is used to characterize risks associated with longer-term exposures of birds to the mancozeb complex.

A major reservation with this approach involves the potential toxicity of ethylenethiourea to birds. As noted in U.S. EPA/OPP/EFED (2011, p. 75), no data are available on the chronic toxicity of ethylenethiourea to birds. As discussed in Section 4.3.1.1.2, the longer-term NOAEL of ethylenethiourea in mammals (0.18 mg/kg bw/day) is substantially below the longer-term NOAEL of mancozeb in mammals (4.83 mg/kg bw/day)—i.e., 4.83 mg/kg bw/day ÷ 0.18 mg/kg bw/day ≈ 26.8. Thus, there is substantial uncertainty about whether or not the NOAEL for mancozeb would be protective for the exposure of birds to the mancozeb complex.

4.3.1.3. Terrestrial Insects

U.S. EPA/OPP risk assessments typically use the honey bee as a surrogate for other species of terrestrial insects. The only toxicity value for the honey bee cited in U.S. EPA/OPP/EFED (2011, p. 73) is an indefinite LD_{50} of >179 µg/bee. This toxicity value is not used by EFED because the LD_{50} is indefinite (U.S. EPA/OPP/EFED 2011, p. 107).

Of greater concern, however, is additional toxicity data on honeybees and other species of insects summarized in Append D of U.S. EPA/OPP/EFED (2011). Specifically, this appendix indicates a foliar residue LD_{50} of 0.27 lb a.i./acre (MRID 00001949) and a reduction in the mean number of eggs hatched per female in *Typhlodromus pyri*, a beneficial predatory mite, at an application rate of 0.02 lb a.i./acre (MRID 45577201). This study is summarized in the main body of the EFED risk assessment as an LR_{50a} of 0.1 lb a.i./acre (pp. 49 and 77) and 0.01 lb a.i./acre (p. 73). The term "LR_{50a}" is not explicitly defined in the EFED risk assessment but appears to refer to the *…residue concentration on foliage causing 50% lethality* (p. 77).

These types of studies on insects are not accommodated in WorksheetMaker. Nonetheless, the Forest Service indicated that an application rate of 1.5 lb a.i./acre will be used. This is above the LOAEL of 0.02 lb a.i./acre by a factor of 75.

As with the EFED risk assessment, the current analysis does not derive a quantitative risk assessment for honey bees. The toxicity data on *Typhlodromus pyri* would need to be addressed, at least qualitatively, in a risk characterization. Nevertheless, the lack of detailed information on this study would impair an interpretation of potential risks to terrestrial insects.

4.3.1.4. Terrestrial Plants

The most recent EPA ecological risk assessment does not quantify risks to terrestrial plants: *Exposures for terrestrial plants are not derived due to the absence of terrestrial plant data to be used in the TerrPlant model* U.S. EPA/OPP/EFED (2011, p. 82).

Furthermore, with regard to the toxicity data on terrestrial plants, the highest tested application rate is 1.38 lb a.i./acre, which is below the highest labelled application rate of 19.1 lbs/acre (U.S. EPA/OPP/EFED 2011, p. 17). This limitation is not a serious concern in the current assessment, because the application rate proposed by the Forest Service is only 1.5 lb a.i./acre. A more serious concern in the current assessment is that the available toxicity data on terrestrial plants involves a formulation of mancozeb that also contains dimethomorph, another fungicide. Specifically, the formulation contains 60% mancozeb and 9% dimethomorph. Despite these limitations, the EPA classifies the studies as "Acceptable" (U.S. EPA/OPP/EFED 2011, Appendix D, pp. 13=14, MRIDs 44283401 and 442834017). [Note: MRID 442834017 is cited only in Appendix D and not in the main document of the EFED risk assessment. The MRID number of 442834017 may just be a typographical error with an unintended "7" at the end. There is probably just a single study.]

In any event, the study or studies appear to be only Tier 1 (single dose) studies and none resulted in a response that exceeded 25%. Thus, as with the EFED risk assessment, risks to terrestrial plants are not quantified in the WorksheetMaker workbook that accompanies the current document.

4.3.2. Aquatic Organisms

As discussed in the following sections, most acute toxicity values are reported in U.S. EPA/OPP/EFED (2011) in units of µg/L. In the WorksheetMaker workbook that accompanies this report, toxicity values are expressed in units of mg/L. In the following sections, toxicity values are generally discussed in units of µg/L to maintain consistency with the EPA source document. All toxicity values used in the WorksheetMaker workbook, however, are also expressed in units of mg/L for clarity, typically in a summary statement.

4.3.2.1 Fish

4.3.2.1.1. Acute Toxicity

U.S. EPA/OPP/EFED (2011, Table 5-1, p. 83) uses an LC_{50} of 460 µg a.i./L to characterize acute risks to aquatic vertebrates. The EPA assessment is specifically focused on the California tiger salamander (*Ambystoma californiense*). Following standard EPA methods, risks to aquatic-phase amphibians are characterized using toxicity data on fish if suitable toxicity data are not available on aquatic-phase amphibians.

As detailed in Appendix D of the EFED risk assessment, the LC_{50} of 460 µg a.i./L for rainbow trout is the lowest reported LC_{50} for mancozeb, and the study is classified by EFED as 'Acceptable' (MRID 40118502, p. 2 of Appendix D). There is a lower LC_{50} of 42 µg a.i./L for trout exposed to maneb (MRID 40706001). Although related to mancozeb, maneb is a different agent. In addition, EFED classifies MRID 40706001 as 'Supplemental' rather than acceptable. Thus, the current assessment defers to EFED and the LC_{50} of 460 µg a.i./L is divided by 20 to approximate an NOAEC of 23 µg a.i./L. This toxicity value is applied to sensitive species of fish—i.e., 0.023 mg a.i./L in Table 7.

Full Forest Service risk assessment also attempt to derive toxicity values for tolerant species of fish (SERA 2014, Sections 1.2.2.2 and 4.3). In Appendix D of the EFED assessment, the highest definitive LC_{50} is 3850 µg a.i./L—i.e., for bluegill sunfish from MRID 000971477. This LC_{50} is divided by 20 to approximate an acute NOAEC of 190 µg a.i./L [3850 µg a.i./L ÷ 20 =192.5 µg a.i./L]. This toxicity value is applied to tolerant species of fish—i.e., 0.19 mg a.i./L in Table 7.

4.3.2.1.2. Longer-term Toxicity

For characterizing risks to fish associated with longer-term exposures to the mancozeb complex, U.S. EPA/OPP/EFED (2011, Table 5-2, p. 85) uses the NOAEC of 2.19 µg a.i./L from a 35-day early life stage study in fathead minnows (MRID 43230701). As specified in Appendix D (p. 3) of the EFED document, the corresponding LOAEC is 4.56 µg a.i./L associated with a decrease in survival and 'lack of growth effects.' No other available studies address the longer-term toxicity of mancozeb to fish.

While the NOAEC of 2.19 µg a.i./L may be viewed as the 'most sensitive' endpoint, it is the only chronic endpoint. No data on the acute toxicity of mancozeb to fathead minnows are summarized in the EFED assessment. Thus, it is not clear if the fathead minnow study should be applied to sensitive or tolerant species.

As discussed further in Section 4.3.2.3.2, however, the NOAEC of 2.19 µg a.i./L in fathead minnows is somewhat lower than the chronic NOAEC in *Daphnia magna*, a presumably sensitive species of aquatic invertebrates. In the absence of any additional information, the NOAEC of 2.19 µg a.i./L in fathead minnows is applied to presumably sensitive species of fish. Risks to more tolerant species of fish are not explicitly characterized. Thus, a longer-term toxicity value for fish of 0.0022 mg a.i./L is included in Table 7 and no toxicity value is given for potentially sensitive species of fish.

4.3.2.2 Amphibians (Aquatic phase)

As discussed in U.S. EPA/OPP/EFED (2011, p. 70), data are not available on the toxicity of mancozeb to aquatic phase amphibians. One open literature publication ((ECOTOX Reference 90116) is available on ethylenethiourea which indicates an NOAEL of 1000 mg a.i./L. As discussed in some detail in the EFED assessment, ethylenethiourea is much less toxic than mancozeb to aquatic species. Consequently, the study on ethylenethiourea, essentially an NOAEC with no corresponding LOAEC, is not useful in the assessment of the toxicity of mancozeb to aquatic phase amphibians.

Consequently and consistent with the approach used in the EFED analysis, a risk characterization of the impact of mancozeb to aquatic phase amphibians would be based on the risk characterization for fish. The only other alternative would be to decline to provide a risk characterization on aquatic phase amphibians.

4.3.2.3. Aquatic Invertebrates

4.3.2.3.1. Acute Toxicity

Relatively little information is available on the toxicity of mancozeb to aquatic invertebrates. The most sensitive acute endpoint is a 48-hour EC_{50} (based on immobility) of 580 µg a.i./L in *Daphnia magna* (U.S. EPA/OPP/EFED 2011, MRID 401185-03, Table 5-3). While classified as 'Acceptable', this study involves static rather than flow-through exposures and the monitored levels of mancozeb decreased during the study. As a conservative method, EFED calculated the EC_{50} based on the concentrations of mancozeb in the test water at the end of the assay. As summarized in the Appendix D of the EFED assessment, a modestly lower EC_{50} of 269 µg a.i./L is available for ethylenethiourea in *Daphnia magna* (MRID 45910302 or 4602090). This study is also classified as 'Acceptable'. Given EFED's approach to the risk assessment of mancozeb (quoted at the start of Section 4.3), it is not clear why the study using ethylenethiourea was not used by EFED for risk characterization. Nonetheless, the current assessment defers to EFED, and the EC_{50} of 580 µg a.i./L for *Daphnia* is divided by 20 to approximate an NOAEC of 29 µg a.i./L [580 µg a.i./L ÷ 20].

The EFED assessment also cites a 10-day LC_{50} of 38.2 mg/kg sediment for *Chironomus dilutus* (i.e., a midge larvae assay, MRID 47101-01). Details of this study (e.g., concentration in pore water) are not given, and this study is not used quantitatively in the EFED assessment.

The estimated NOAEC of 29 µg a.i./L for *Daphnia magna* is used in the current assessment (i.e., 0.029 mg a.i./L in Table 7). Given the limited information on the toxicity of mancozeb, it is not clear if *Daphnia magna* should be viewed as a sensitive or tolerant species. The EC_{50} of 580 µg a.i./L is similar to the LC_{50} of 460 µg a.i./L in trout, a sensitive species of fish. In addition, as discussed in the following section, the chronic toxicity of mancozeb to *Daphnia magna* suggests that daphnids are highly sensitive to mancozeb. Thus, *Daphnia magna* is viewed as a potentially sensitive species, and risks to tolerant species of freshwater invertebrates are not explicitly characterized.

4.3.2.3.2. Chronic Toxicity

U.S. EPA/OPP/EFED (2011, Table 5-4, p. 89) uses a 21-day NOAEC of 7.3 µg a.i./L for *Daphnia magna* (MRID 409538-02) to characterize risks to aquatic invertebrates from longer-term exposures to the mancozeb complex. Although this study is not included in Appendix D of the EFED assessment, the main body of the EFED assessment (p. 68) notes that the study is classified as 'Acceptable'.

Appendix D (p. 4) of the EFED assessment cites an NOAEC of 2 µg a.i./L in a reproduction study in *Daphnia magna* using ethylenethiourea (MRID 45462901). This study is classified as 'Supplemental' rather than 'Acceptable'. As with the acute toxicity values for aquatic invertebrates, the toxicity values associated with ethylenethiourea are somewhat lower than those associated with mancozeb. Again, the failure to use the lower of the toxicity values for mancozeb and ethylenethiourea appears to be contrary to the EFED approach, as quoted at the start of Section 4.3 of the current document. Perhaps, one reason for not using the lower NOAEC for ethylenethiourea (relative to mancozeb in terms of chronic effects in aquatic invertebrates) involves the classification of the ethylenethiourea study as 'Supplemental.' EFED prefers to use studies classified as 'Acceptable' rather than 'Supplemental' for deriving risk values. As noted above, the chronic daphnid study with mancozeb is classified as 'Acceptable'.

4.3.2.4. Aquatic Plants

4.3.2.4.1. Algae

The EPA risk summary table for aquatic plants (U.S. EPA/OPP/EFED 2011, Table 5-5, pp. 89-90) does not specify either the selected toxicity value or the study. Given the peak EEC values and the reported RQs, however, the toxicity value is about 13.7 µg a.i./L. The concentration of 13.7 µg a.i./L is the reported EC_{50} for *Navicula pelliculosa* from MRID 44283402. The NOAEC is specified as 2.88 µg a.i./L. In Appendix D of the EFED assessment, the agent used in this study is specified as an end-use formulation of 9% a.i. dimethomorph/zoxamide and 60% mancozeb, and the concentration of 13.7 µg a.i./L is defined as the "*total product concentration*". It is not clear if the term "*total product concentration*" refers to the total concentration of dimethomorph/zoxamide and mancozeb or to the formulation—i.e., these compounds plus other ingredients. The current assessment defers to EFED and does not adjust the concentration for mancozeb alone.

As noted previously, the Forest Service risk assessments prefers to use NOAEC values rather than EC_{50} or other similar toxicity values in their risk assessments. Accordingly, the NOAEC of 2.88 µg a.i./L is used in the current assessment. Based on other toxicity data in Appendix D of the EFED assessment, *Navicula pelliculosa* is clearly a sensitive species, and the NOAEC of 0.00288 mg a.i./L is included in Table 7 for sensitive species of algae.

Appendix D of the EFED assessment also summarizes an assay using Maneb (another EBDC pesticide) in *Pseudokirchneriella subcapitata* with a reported EC_{50} of 13.4 µg a.i./L and a corresponding NOAEC of 5 µg a.i./L (MRID 40943501). While the EC_{50} of 13.4 µg a.i./L is somewhat below the 13.7 µg a.i./L apparently used by EFED, the NOAEC of 5 µg a.i./L in *Pseudokirchneriella subcapitata* is higher than the NOAEC of 2.88 a.i./L in *Navicula pelliculosa*.

4.3.2.4.1.2. Tolerant Species

Based on the studies summarized in Appendix D of the EFED assessment, the most tolerant species of algae is *Anabaena flos-aquae*, a freshwater blue-green alga. The EC_{50} for this species is 130 µg a.i./L with an NOAEC of 28 µg a.i./L (MRID 44283402). Note that this MRID is identical to the study in *Navicula pelliculosa* and the description of the test material from this study applies to the assay on *Anabaena flosaquae*. In Table 7, the NOAEC of 0.028 mg a.i./L is use to characterize risks in tolerant species of algae.

4.3.2.4.2. Aquatic Macrophytes

The EFED assessment does not explicitly develop a dose-response value for aquatic macrophytes: *Due to the absence of toxicity studies for vascular plants, the algal data will be used as a surrogate to represent indirect effects for both vascular and nonvascular aquatic plants*" (U.S. EPA/OPP/EFED 2011, p. 16). This approach is used in the current assessment.

4.4. Risk Characterization

4.4.1. Terrestrial Organisms

4.4.1.1. Mammals

The risk characterization for mammals is summarized in Worksheet G02a. As summarized in Table 7, the acute HQs (both accidental and non-accidental) are based on the toxicity of mancozeb, and the longer-term HQs are based on the toxicity of ethylenethiourea. As discussed in Sections 3.3 and 4.3.1.1, this approach parallels the one taken in U.S. EPA/OPP/HED (2013a).

None of the acute HQs exceeds the level of concern. In addition, none of the longer-term HQs associated with the contamination of surface water exceeds the level of concern.

All of the central estimates and upper bounds of the chronic HQs associated with the consumption of contaminated vegetation exceed the level of concern, and some of the exceedances are substantial—e.g., an upper bound HQ of 2015 for the consumption of contaminated short grass by a 20 gram mammal. Furthermore, several of the lower bound HQs also exceed the level of concern—e.g., a lower bound HQ of 15 for the consumption of contaminated short grass by a 20 gram mammal.

As discussed in SERA (2014a), chronic HQs are based on the underlying exposure assumption that 100% of the diet is contaminated. Given that only 7 acres of the nursery are treated with mancozeb, the assumption that 100% of the diet is contaminated may not be reasonable for most (if any) mammals. If this were the case, the residue rates in Worksheets B05a-d could be adjusted downward based on reasonable estimates of the proportion of an animal's diet that might be contaminated. While somewhat *ad hoc*, the simplest way to make this adjustment uniformly would be to use the "*Drift*" factors in Worksheet A01.

Notwithstanding the potential to refine the exposure assessment using a dietary contamination of less than 100%, some of the chronic HQs are extremely high and reasonable adjustments to the percentage of dietary contamination would probably not reduce all HQs to below the level of concern (HQ=1).

4.4.1.2. Birds

The risk characterization for birds is summarized in Worksheet G02b. As summarized in Table 7, both acute and longer-term HQs are based on the toxicity mancozeb. As discussed in Section 4.3.1.2, the toxicity values are based on the values used in U.S. EPA/OPP/EFED (2011).

As with mammals, none of the HQs associated with the consumption of contaminated water exceeds the level of concern. Several of the acute and chronic HQs associated with the consumption of contaminated vegetation exceed the level of concern at both the central estimates and the upper bounds. The magnitudes of the exceedances, however, are much less than those for mammals. The highest HQ is 186, the upper bound of the HQ for the longer-term consumption of contaminated short-grass by a small bird. While this is a standard exposure scenario in Forest Service risk assessments, the scenario may not be relevant to most species of small birds. In addition, because of the lower HQs for birds, relative to mammals, considerations of the proportion of the diet that is contaminated (as discussed in Section 4.4.1.1) may be useful in refining the risk characterization.

4.4.1.3. Terrestrial Insects

Risks to terrestrial insects could probably be addressed qualitatively based on the LOAEL of 0.02 lb a.i./acre. This LOAEL is not discussed in great detail in the EPA risk assessment (U.S. EPA/OPP/EFED 2011). Also, given the limited use of mancozeb at the JH Stone Nursery, any effects on terrestrial insects would be highly localized.

4.4.2. Aquatic Organisms

The HQs for aquatic organisms are summarized in Worksheet G03. None of the non-accidental HQs exceeds the level of concern (HQ=1). The highest HQ is 0.009. This is the upper bound HQ for the longer-term exposure in sensitive species of fish, and this HQ is below the level of concern by a factor of over 110 [1 ÷ 0.009 ≈ 111.11]. Thus, there is no basis to assert that the planned use of mancozeb will adversely impact aquatic organisms.

All of the accidental exposure scenarios substantially exceed the level of concern with HQs of up to 1183, the upper bound HQ for sensitive species of algae. As detailed in Worksheet A01, this scenario is based on the spill of 100 (20 to 200) gallons of a field solution. Given that 7 acres are treated at an application volume of 30 gallons/acre, the upper bound of the spill is near to the maximum volume of the mancozeb solution to be used at the JH Stone Nursery. Nonetheless, given the magnitude of the lower bound of HQs in worksheet G03, even a modest spill might adversely affect aquatic organisms.

5. REFERENCES

5.1. Chemical Specific References

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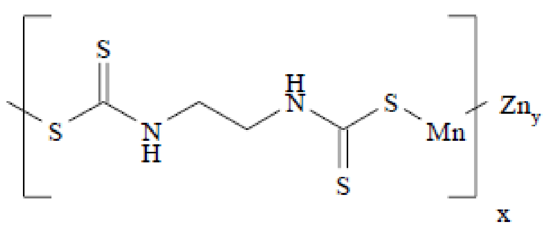
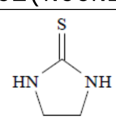
Table 1: Chemical and Physical Properties

Item	Value	Reference[1]
	Identifiers	
Common name:	Mancozeb	
CAS Name	[[1,2-ethanediylbis[carbamodithioato]](2-)]manganese mixture with [[1,2- Ethanediylbis [carbamodithioato]](2-)]zinc	Tomlin 2004
CAS No.	8018-01-7 [formerly 8065-67-6]	Tomlin 2004
Chemical Group	Ethylenebis dithiocarbamate	U.S. EPA/OPP/HED 2013, p. 4
Compostion	The ISO definition is 'a complex of zinc and maneb containing 20% of manganese and 2.55% of zinc, the salt present being stated (for instance mancozeb chloride)'. A manufacturer gives the ratio of maneb to zinc as 1:0.091, i.e. 20% Mn and 2.2% Zn.	Tomlin 2004
Formulations	Dithane 45®, Manzate 200®, Penncozeb®, Fore and more	U.S. EPA/OPP 2005a, p. 4; U.S. EPA/OPP/HED 2013, p. 12
IUPAC Name	manganese ethylenebis(dithiocarbamate) (polymeric) complex with zinc salt	Tomlin 2004
Molecular formula	$[C_4H_6MnN_2S_4]_xZn_y$	Tomlin 2004; U.S. EPA/OPP 2005a, p. 4
Mechanistic group	Disrupts lipid metabolism, respiration, and ATP production	Tomlin 2004
EPA PC Code	014504	U.S. EPA/OPP/EFED 2011
Structure	 Note: U.S. EPA/OPP/EFED 2011, Table 2-1 specifies X:Y 10:1.	U.S. EPA/OPP 2005a, p. 4
Use	Fungicide	Tomlin 2004
	Chemical Properties(1)	
Aqueous photolysis	Stable	U.S. EPA/OPP/EFED 2011, Table 2-1
Hydrolysis, $t_{½}$	**DT_{50}** – **pH at 25°C** 20 days – 5 17 hours – 7 34 hours – 9	Tomlin 2004
	0.7 days (17 hours) at pH 7	U.S. EPA/OPP/EFED 2011, Table 2-1
	4 days (90^{th} percentile of 0.8, 0.7, and 1.4)	U.S. EPA/OPP/EFED 2011, Table 3-2
K_{ow}	1.8 [logP = 0.26]	Tomlin 2004
	3.24	U.S. EPA/OPP/HED 2013
Molecular weight (g/mole)	271.2 (see *Composition* above)	Tomlin 2004
	(265.3)x + (65.4)y	U.S. EPA/OPP 2005a, p. 4
	271	U.S. EPA/OPP/EFED 2011, Table 2-1
Melting point	Decomposes at 172 °C	Tomlin 2004

Item	Value	Reference[1]
Soil Photolysis	Stable	U.S. EPA/OPP/EFED 2011, Table 2-1
Vapor pressure	<1.33x 10^{-2} mPa (20 °C)	Tomlin 2004
	Negligible.	U.S. EPA/OPP/HED 2013
	1.003xe^{-7}	U.S. EPA/OPP/EFED 2011, Table 3-2
Water solubility	6.2 ppm (pH 7.5, 25 °C)	Tomlin 2004
	6-20 mg/L	U.S. EPA/OPP/EFED 2011, Table 2-1
	6 mg/L	Knisel and Davis 2000
	6 mg/L	U.S. EPA/OPP/EFED 2011, Table 3-2
	Environmental Properties	
Aerobic soil metabolism	164 days (90^{th} percentile of 121, 161, and 143)	U.S. EPA/OPP/EFED 2011, Table 3-2
Bioconcentration in fish (BCF)	3.162 L/kg wet-wt	EPI Suite 2011
Bio-lyses, water, $t_{½}$	682 days (upper 90^{th} percentile of 11 and 391)	U.S. EPA/OPP/EFED 2011, Table 3-2
Bio-lyses, sediment, $t_{½}$	276 days (one value of 92 x 3)	U.S. EPA/OPP/EFED 2011, Table 3-2
Field dissipation		
Foliar washoff fraction	0.25	Knisel and Davis 2000
Foliar half-life	10 days	Knisel and Davis 2000
	20 days	U.S. EPA/OPP/EFED 2011, p. 64
K_{oc}	2000	Knisel and Davis 2000
	1,167 (average, NOS)	U.S. EPA/OPP/EFED 2011, Table 3-2
	860-1,642	U.S. EPA/OPP/EFED 2011, p. 28
Soil half-life (NOS)	70 days	Knisel and Davis 2000
	Ethylenethiourea (Major Degradate)	
Identity	Ethylenethiourea (a.k.a. 2-Imidazolidinethione)	U.S. EPA/OPP 2005a U.S. EPA/OPP/HED 2013
CAS Number	96-45-7	U.S. EPA/OPP 2005a U.S. EPA/OPP/HED 2013
Henry's Law Constant	1.36x10^{-11} atm-m^3/mole	ChemIDplus 2014
K_{oc}	288 (highly mobile)	U.S. EPA/OPP/EFED 2011, p. 28
K_{ow}	0.21 [log P = -0.66], experimental	ChemIDplus 2014; EPI Suite 2011
Molecular weight	102.1604	ChemIDplus 2014
Smiles notation	`C1(NCCN1)=S`	ChemIDplus 2014
Structure		U.S. EPA/OPP 2005a U.S. EPA/OPP/HED 2013
Vapor pressure	2.02x10^{-6} mm Hg	ChemIDplus 2014
Water solubility	20,000 mg/L (experimental)	U.S. EPA/OPP/EFED 2011, p. 28; EPI Suite 2011

See Section 2 for discussion.

Table 2: Ethylenethiourea Inputs and Outputs for FIRST Simulations

Parameter	Central Estimate of Concentration in Water	Lower Bound of Concentration in Water	Upper Bound of Concentration in Water
Aerobic soil metabolism half-life (days) [1]	143	121	164
Aerobic aquatic metabolism (days) [2]	391	11	682
K_{oc} (mL/g) [3]	1251	1642	860
Photolysis half-life (days) [4]	Stable	Stable	Stable
Water solubility (mg/L) [4]	6	6	6
WCR Peak Concentration (µg/L per lb/acre)	2.68	2.37	3.169
WCR Longer-term Concentration (µg/L per lb/acre)	0.984	0.132	0.679
Proportion of Treated Watershed [5]	0.032		
Peak Concentration Used in Analysis (µg/L per lb/acre)	0.086	0.076	0.101
Longer-term Concentration Used in Analysis (µg/L per lb/acre)	0.031	0.004	0.022

Other General Inputs: Application rate: **0.075 lb/acre**, 1 application; Proportion of watershed treated: 1.0; Wetted in: No; Drift: None; Incorporation Depth: 0 cm.

[1] Central and lower estimates from values in Table 1 with upper bound from EPA analysis.

[2] Central estimate and range from EPA values for biolysis in water in Table 1 of this document.

[3] Upper and lower bounds from U.S. EPA/OPP/EFED 2011, p. 28 with the central estimate as the average of this range. See Table 1 of this document for references. Note that lower bound K_{oc} is used for upper bound estimate and upper bound Koc value is used for lower bound estimate.

[4] U.S. EPA/OPP/EFED 2011, Table 3-2.

[5] Section 2.

SPECIAL NOTE: The application rate of 0.075 is used to account for 7.5% conversion of mancozeb to ethylenethiourea (U.S. EPA/OPP/HED 2013a, p. 36).

See Section 3.2. for discussion.
See Appendix 1 for output files.

Table 3: Total Toxic Residues in Surface Water from EFED Modeling

Crop (s) Represented	**MAR** *Maximum Application Rate (kg/ha)*	**MNA** *Maximum Number of Applications*	**Total Cumulative Application Rate (lb/ac) [MAR x MNA x 0.892]**	*Peak (short-term) Conc. (µg/L)*	*Longer Term Conc. (µg/L)*	**Peak WCR µg/L per lb a.i./acre**	**Longer-term WCR µg/L per lb a.i./acre**
Apple, crab apple, etc.	5.381	4	19.199408	13.44	2.23	0.70002	0.11615
Asparagus	1.794	4	6.400992	17.23	3.21	2.69177	0.50148
Cereal Grains 1	1.794	3	4.800744	30.35	5.85	6.32194	1.21856
Corn (Field.seed crop)	1.345	10	11.9974	51.72	7.40	4.31093	0.61680
Corn (Sweet/Pop)	1.345	5	5.9987	24.16	3.40	4.02754	0.56679
Corn (Sweet/Pop)	1.345	10	11.9974	74.33	11.11	6.19551	0.92603
Corn (Sweet/Pop)	1.345	20	23.9948	147.65	26.82	6.15342	1.11774
Cotton	1.794	4	6.400992	13.12	2.62	2.04968	0.40931
Cucurbits 2	2.690	8	19.19584	40.64	6.17	2.11713	0.32142
Cucurbits, Others 3	2.690	8	19.19584	40.64	6.17	2.11713	0.32142
Fennel (one crop)	1.794	8	12.801984	8.01	3.62	0.62568	0.28277
Fennel (two crops)	1.794	16	25.603968	18.11	5.63	0.70731	0.21989
Forestry (Douglas Fir)	3.587	3	9.598812	44.89	7.64	4.67662	0.79593
Garlic	2.690	10	23.9948	41.93	13.76	1.74746	0.57346
Ginseng	1.682	12	18.004128	14.51	0.73	0.80593	0.04055
Grapes	2.242	3	5.999592	13.50	2.34	2.25015	0.39003
Grapes (Wine)	2.242	3	5.999592	14.60	3.07	2.43350	0.51170
Onion (dry) & Shallot	2.690	10	23.9948	12.79	6.24	0.53303	0.26006
Ornamentals, nursery	1.569	5	6.99774	33.29	5.36	4.75725	0.76596
Ornamentals	1.569	5	6.99774	1.77	0.39	0.25294	0.05573
Ornamentals	19.505	5	86.9923	22.68	4.28	0.26071	0.04920
Residential turf	21.411	4	76.394448	24.18	4.48	0.31652	0.05864
Papayas	2.242	14	27.998096	38.43	4.51	1.37259	0.16108
Potatoes	1.794	7	11.201736	12.37	3.46	1.10429	0.30888
Sugar beet	1.794	7	11.201736	12.27	4.10	1.09537	0.36601
Tomatoes	1.794	4	6.400992	11.81	3.07	1.84503	0.47961
Tropical fruits	2.096	14	26.174848	43.03	1.44	1.64394	0.05501
Tropical Fruits	2.240	14	27.97312	5.58	0.14	0.19948	0.00500
Turf	21.411	4	76.394448	125.50	30.69	1.64279	0.40173
Turf	21.411	8	152.7889	190.0	59.55	1.24355	0.38975
X-mass trees	3.587	3	9.598812	44.89	7.64	4.67662	0.79593

Summary

Average	2.29	0.422
5% Lower Bound	1.73	0.328
95% Upper Bound	2.84	0.514

See Section 3.2.2.1 for data sources, analysis and discussion.

Table 4: Estimated of Total Toxic Residues in Surface Water Used in the Current Assessment

Parameter	Central Estimate of Concentration in Water	Lower Bound of Concentration in Water	Upper Bound of Concentration in Water
WCR Peak Concentration (µg/L per lb/acre)	2.29	1.73	2.84
WCR Longer-term Concentration (µg/L per lb/acre)	0.422	0.328	0.516
Proportion of Treated Watershed [5]	0.032		
Peak Concentration Used in Analysis (µg/L per lb/acre)	0.073	0.055	0.091
Longer-term Concentration Used in Analysis (µg/L per lb/acre)	0.014	0.01	0.017

See Table 3 for WCR values.
See Appendix 2 for calculation of peak WCRs.
See Appendix 3 for calculation of peak WCRs.
See Section 3.2.2.1 for discussion.

Table 5: Mancozeb, summary of toxicity values used in human health risk assessment

Acute – single exposure, general public (including men)

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2013a, Table 4.3.1, p. 23
NOAEL Dose	500 mg/kg bw
LOAEL Dose	1000 mg/kg bw
LOAEL Endpoint(s)	Decreased motor activity
Uncertainty Factor	100
Acute RfD, general public	5 mg/kg bw/day
Note	Used in current document for acute occupational exposures (males) and acute exposures to the general public in food (males).

Acute – single exposure, females

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2013a, Table 4.3.1, p. 23
NOAEL Dose	128 mg/kg bw
LOAEL Dose	512 mg/kg bw
LOAEL Endpoint(s)	Hydrocephaly and other malformations.
Uncertainty Factor	100/1000
Acute RfD	0.13 mg/kg bw/day
Population Adjusted Dose	0.013 mg/kg bw/day
Note	Used in current document for acute occupational exposures (females) and acute exposures to the general public in food (females).

Chronic – General population

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2013a, Table 4.3.1, p. 24
NOAEL Dose	4.83 mg/kg bw/day
LOAEL Dose	30.9 mg/kg bw/day
LOAEL Endpoint(s)	Toxicity to the thyroid.
Uncertainty Factor	300
Equivalent RfD	0.16 mg/kg bw/day (applicable to men)
Population Adjusted Dose	0.016 mg/kg bw/day for 13-49 year old females
Note	Used in the current assessment only for longer-term exposures involving the consumption of contaminated food. The population adjusted dose is handled in WorksheetMaker workbook.

(*Continued on next page*)

Table 5 (*continued*)

Carcinogenicity

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2013a, p. 23
Cancer Potency	0.0601 (mg/kg bw/day)$^{-1}$ x 0.075 = 0.0045 mg/kg bw/day (mg/kg bw/day)$^{-1}$ The dose associated with a risk of 1-in-1 million is [Risk=Potency x Dose; Dose = Risk/Potency; 0.000001÷0.0045 = 0.00022 mg/kg bw/day]
Note:	Used in the current assessment to assess cancer risks associated with the consumption of contaminated food.

Occupational – 1 to 6 month exposure periods

As discussed in Section 3.2.1.1, worker risks are characterized for ethylenethiourea rather than mancozeb.

See Section 3.3 for discussion.

Table 6: Ethylenethiourea, summary of toxicity values used in human health risk assessment

Acute – single exposure

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2013a, Table 4.3.2, p. 25
NOAEL Dose	5 mg/kg bw/day
LOAEL Dose	10 mg/kg bw/day
LOAEL Endpoint(s)	Hydrocephaly and other malformations
Uncertainty Factor	100
Equivalent RfD	0.05 mg/kg bw/day
Population Adjusted Dose	0.005 mg/kg bw/day for 13-49 year old females.
Note:	For the general public, the population adjusted dose is handled in standard WorksheetMaker workbook.

Chronic – lifetime exposure

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2013a, Table 4.3.2, p. 25
NOAEL Dose	0.18 mg/kg bw/day
LOAEL Dose	1.99 mg/kg bw/day
LOAEL Endpoint(s)	Thyroid toxicity
Uncertainty Factor	100
Equivalent RfD	0.0018 mg/kg bw/day
Population Adjusted Dose	0.00018 mg/kg bw/day for females 13-49 years old.
Note:	This toxicity value is used for members of general public in exposure scenarios involving surface water and the consumption of contaminated fish.

Carcinogenicity

Element	Derivation of RfD
EPA Document	U.S. EPA/OPP/HED 2013a, p. 23
Cancer Potency	0.0601 (mg/kg bw/day)$^{-1}$ The dose associated with a risk of 1-in-1 million is [Risk=Potency x Dose; Dose = Risk/Potency; 0.000001÷0.0601 = 0.000017 mg/kg bw/day]
Note:	Used in the current assessment to assess cancer risks associated with the consumption of contaminated water.

See Section 3.3 for discussion.

Table 7: Summary of toxicity values used in ecological risk assessment

Group/Duration Organism		Endpoint	Toxicity Value (a.i.)	Reference
Terrestrial Animals				
Acute				
	Mammals (including canids)	NOAEL, mancozeb	500 mg/kg bw	Section 4.3.1.1.1.
	Birds	LD_{50}÷20, mancozeb	150 mg/kg bw	Section 4.3.1.2.1.
	Terrestrial Insects	LOAEL, beneficial mite	0.02 lb a.i./acre	Section 4.3.2.4.1
Longer-term				
	Mammals	NOAEL, ethylenethiourea	0.18 mg/kg bw/day	Section 4.3.1.1.2.
	Bird	NOAEL, mancozeb	4.83 mg/kg bw/day	Section 4.3.2.2.
Aquatic Animals		All values for mancozeb.		
Acute				
Fish	Sensitive	Trout LC_{50} ÷ 20	0.023 mg/L	Section 4.3.2.1.1
	Tolerant	Bluegill LC_{50} ÷ 20	0.19 mg/L	Section 4.3.2.1.1
Invertebrates	Sensitive	Daphnia EC_{50} ÷ 20	0.029 mg/L	Section 4.3.2.3.1
	Tolerant	No suitable data.	N/A	Section 4.3.2.3.1
Longer-term				
Fish	Sensitive	Fathead minnow NOAEC	0.0022 mg/L	Section 4.3.2.1.2.
	Tolerant	No suitable data.	N/A	Section 4.3.2.1.2.
Invertebrates	Sensitive	Daphnia NOAEC	0.0073 mg/L	Section 4.3.2.3.3
	Tolerant	No suitable data.	N/A	Section 4.3.2.3.3
Aquatic Plants				
Algae	Sensitive	*Navicula pelliculosa*	0.00288 mg/L	Section 4.3.2.4.1.1
	Tolerant	*Anabaena flos-aquae*	0.028 mg/L	Section 4.3.2.4.1.2.
Macrophytes	Sensitive	No suitable data.	N/A	Section 4.3.2.4.2
	Tolerant	No suitable data.	N/A	Section 4.3.2.4.2

Appendix 1: FIRST Runs for Ethylenethiourea following Mancozeb Application

Central Estimate

```
RUN No.   1 FOR Mancozeb         ON   None          * INPUT VALUES *
--------------------------------------------------------------------
 RATE (#/AC)   No.APPS &   SOIL  SOLUBIL  APPL TYPE  %CROPPED INCORP
  ONE(MULT)    INTERVAL    Koc   (PPM )   (%DRIFT)     AREA    (IN)
--------------------------------------------------------------------
0.075(  0.075)   1   1    1251.0    6.0   GRANUL( 0.0) 100.0   0.0

FIELD AND RESERVOIR HALFLIFE VALUES (DAYS)
--------------------------------------------------------------------
METABOLIC  DAYS UNTIL  HYDROLYSIS   PHOTOLYSIS   METABOLIC  COMBINED
 (FIELD)  RAIN/RUNOFF  (RESERVOIR)  (RES.-EFF)   (RESER.)   (RESER.)
--------------------------------------------------------------------
 143.00        2           0.00    0.00-    0.00  391.00     391.00

UNTREATED WATER CONC (MICROGRAMS/LITER (PPB)) Ver 1.1.1  MAR 26, 2008
--------------------------------------------------------------------
     PEAK DAY  (ACUTE)      ANNUAL AVERAGE (CHRONIC)
       CONCENTRATION             CONCENTRATION
--------------------------------------------------------------------
           2.677                      0.984
```

Lower Bound

```
RUN No.   1 FOR Mancozeb         ON   None          * INPUT VALUES *
--------------------------------------------------------------------
 RATE (#/AC)   No.APPS &   SOIL  SOLUBIL  APPL TYPE  %CROPPED INCORP
  ONE(MULT)    INTERVAL    Koc   (PPM )   (%DRIFT)     AREA    (IN)
--------------------------------------------------------------------
0.075(  0.075)   1   1    1642.0    6.0   GRANUL( 0.0) 100.0   0.0

FIELD AND RESERVOIR HALFLIFE VALUES (DAYS)
--------------------------------------------------------------------
METABOLIC  DAYS UNTIL  HYDROLYSIS   PHOTOLYSIS   METABOLIC  COMBINED
 (FIELD)  RAIN/RUNOFF  (RESERVOIR)  (RES.-EFF)   (RESER.)   (RESER.)
--------------------------------------------------------------------
 121.00        2           0.00    0.00-    0.00   11.00      11.00

UNTREATED WATER CONC (MICROGRAMS/LITER (PPB)) Ver 1.1.1  MAR 26, 2008
--------------------------------------------------------------------
     PEAK DAY  (ACUTE)      ANNUAL AVERAGE (CHRONIC)
       CONCENTRATION             CONCENTRATION
--------------------------------------------------------------------
           2.370                      0.132
```

Upper Bound

```
RUN No.   1 FOR Mancozeb         ON   None          * INPUT VALUES *
--------------------------------------------------------------------
 RATE (#/AC)   No.APPS &   SOIL  SOLUBIL  APPL TYPE  %CROPPED INCORP
  ONE(MULT)    INTERVAL    Koc   (PPM )   (%DRIFT)     AREA    (IN)
--------------------------------------------------------------------
0.075(  0.075)   1   1     860.0    6.0   GRANUL( 0.0) 100.0   0.0

FIELD AND RESERVOIR HALFLIFE VALUES (DAYS)
--------------------------------------------------------------------
METABOLIC  DAYS UNTIL  HYDROLYSIS   PHOTOLYSIS   METABOLIC  COMBINED
 (FIELD)  RAIN/RUNOFF  (RESERVOIR)  (RES.-EFF)   (RESER.)   (RESER.)
--------------------------------------------------------------------
 164.00        2           0.00    0.00-    0.00  682.00     682.00

UNTREATED WATER CONC (MICROGRAMS/LITER (PPB)) Ver 1.1.1  MAR 26, 2008
--------------------------------------------------------------------
     PEAK DAY  (ACUTE)      ANNUAL AVERAGE (CHRONIC)
       CONCENTRATION             CONCENTRATION
--------------------------------------------------------------------
           3.169                      0.679
```

Appendix 2: 90% Confidence Interval for peak WCRs of mancozeb residues

Item Number	Value	Square of Error
1	0.70002	2.516338
2	2.69177	0.164392
3	6.32194	16.286253
4	4.31093	4.099058
5	4.02754	3.031858
6	6.19551	15.281790
7	6.15342	14.954486
8	2.04968	0.055997
9	2.11713	0.028624
10	2.11713	0.028624
11	0.62568	2.757715
12	0.70731	2.493263
13	4.67662	5.713548
14	1.74746	0.290367
15	0.80593	2.191546
16	2.25015	0.001308
17	2.4335	0.021663
18	0.53303	3.074015
19	4.75725	6.105510
20	0.25294	4.134622
21	0.26071	4.103084
22	0.31652	3.880100
23	1.37259	0.834897
24	1.10429	1.397188
25	1.09537	1.418355
26	1.84503	0.194734
27	1.64394	0.412648
28	0.19948	4.354889
29	1.64279	0.414127
30	1.24355	1.087363
31	4.67662	5.713548
Average	**2.286317**	
SSE	107.041910	
Sample Standard Deviation	1.888932	
Critical Value of t at 0.1	1.645	
Value of 5% Lower Bound	**1.7282307**	
Value of 95% Upper Bound	**2.8444033**	

See Table 3 details of data.
See Section 3.2.2.1 for discussion.

Appendix 3: 90% Confidence Interval for longer-term WCRs of mancozeb residues

Item Number	Value	Square of Error
1	0.11615	0.093556
2	0.50148	0.006314
3	1.21856	0.634476
4	0.6168	0.037939
5	0.56679	0.020958
6	0.92603	0.254026
7	1.11774	0.484026
8	0.40931	0.000162
9	0.32142	0.010120
10	0.32142	0.010120
11	0.28277	0.019391
12	0.21989	0.040857
13	0.79593	0.139809
14	0.57346	0.022934
15	0.04055	0.145519
16	0.39003	0.001023
17	0.5117	0.008043
18	0.26006	0.026231
19	0.76596	0.118295
20	0.05573	0.134168
21	0.0492	0.138995
22	0.05864	0.132045
23	0.16108	0.068090
24	0.30888	0.012801
25	0.36601	0.003137
26	0.47961	0.003317
27	0.05501	0.134696
28	0.005	0.173906
29	0.40173	0.000412
30	0.38975	0.001041
31	0.79593	0.139809
Average	**0.422020**	
SSE	3.016216	
Sample Standard Deviation	0.317081	
Critical Value of t at 0.1	1.645	
Value of 5% Lower Bound	**0.3283382**	
Value of 95% Upper Bound	**0.5157018**	

See Table 3 details of data.
See Section 3.2.2.1 for discussion.