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OFFICE OF CHEMICAL SAFETY AND POLLUTION PREVENTION

MEMORANDUM

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Preface

The Environmental Fate and Effects Division (EFED) has conducted a draft ecological risk assessment (DRA), as well as a drinking water assessment (DWA), in support of the Registration Review of the conventional uses of the fumigant methyl bromide. The decision not to conduct a full quantitative risk assessment was made together with the Pesticide Re-evaluation Division (PRD) and was based primarily on an evaluation of the data submitted since the last major risk assessment for this compound.

Methyl bromide uses are currently being reduced as a result of the Montreal Protocol of 1987, which mandated the phase-out of all ozone depleting substances, like methyl bromide, by January 1, 2005. The phase-out effectively prohibits the manufacturing and importation of methyl bromide in the United States. From 1998 to 2013 crop usage declined from approximately 60 million lbs active to 7.5 million pounds of active used per year. However, the Montreal Protocol allowed for certain exemptions from the manufacturing and importation restrictions for certain uses of methyl bromide, which were enacted on January 1, 2005. The first exemption is known as a critical use exemption (CUE) which applies to pre-plant soil fumigation uses. The second exemption allowed under the Montreal Protocol for methyl bromide use is known as a quarantine and pre-shipment (QPS) exemption. In general, this latter exemption applies for the use of methyl bromide on food and commodities stored in buildings or cargo holds that are imported and eventually distributed domestically, or exported to other countries from the U.S. 2013 estimates for CUE and QPS usage were approximately 5.2 million pounds and this level of usage was expected to continue.

Risk Management Objectives

EPA is taking a streamlined approach for this assessment by utilizing much of the analysis previously performed for the 2013 Problem Formulation¹. This allows EPA to conserve Agency resources and avoid redundancy with previous assessments. The majority of the environmental fate and ecotoxicological data needed to evaluate ecological risk under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), was previously evaluated for the assessment to support the Reregistration Eligibility Decision (RED)². Following the publication of the Problem Formulation, the Data Call-In (DCI) for methyl bromide required data for non-target plants and honey bees (vapor phase exposure), that were subsequently submitted, evaluated, and incorporated into this risk assessment.

¹ Problem Formulation for the Environmental Fate, Ecological Risk, Endangered Species, and Drinking Water Exposure Assessments in Support of the Registration Review for Methyl Bromide (DP Barcode: 410209 dated September 20, 2013)

² Revised Draft Methyl Bromide Environmental Fate and Ecological Risk Assessment - following the review of 30-Day Error Correction Comments Code 053201; DP Code 311406 June 5, 2005.

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1.0 Executive Summary

This draft ecological risk assessment (DRA) and drinking water assessment (DWA) was developed in support of the Registration Review of the multi-use fumigant methyl bromide. In order to better understand the potential routes of exposure a use characterization has been included in this summary.

For reasons discussed below, estimated drinking water concentrations and estimated exposure concentrations (EDWCs and EECs, respectively) were not developed, and therefore risk quotients (RQs) were not estimated. It should be noted that while newly submitted environmental fate and ecological effects data have not been used to update previously determined RQs or EDWCs, they have provided more certainty in the risk and exposure conclusions discussed below.

1.1 Ecological Risk from Current Uses to Aquatic Organisms

Volatilization is a main route of dissipation for methyl bromide and as a result, the potential movement from leaching and runoff to aquatic habitats is considered low. Additionally, the conversion of methyl bromide in water is rapid (aquatic dissipation half-life of 72 minutes (Nelly et al., 1976)), thus potential aquatic exposure time is significantly reduced. Washout from air by rainfall and deposition in receiving waterbodies could occur, but the rate of deposition would likely be limited by atmospheric conditions (precipitation and settling of dry particulates) and delivery to the water interface.

Due to the volatile nature (*i.e.*, vapor pressure, Henry's Law Constant) of this compound, the injection methods used for application, and the use of tarps over most treated sites, the potential for methyl bromide to be present in runoff from a treated agricultural field to adjacent waterbodies is expected to be very low. The low octanol/water partition coefficients of methyl bromide (log $K_{ow} = 1.18$) indicates it is not likely to bioconcentrate in tissues of aquatic organisms. As a result, acute and chronic risk from aquatic organism exposure is expected to be low.

1.2 Ecological Risk from Current Uses to Terrestrial Organisms

As volatilization of methyl bromide from treated surfaces is significant and occurs rapidly, inhalation of and direct dermal or surface contact to drifting vapors are expected to be the main potential exposure routes to animals and terrestrial plants. This exposure path will be limited in applications in which tarps are applied after the shank injection equipment and gases are trapped until tarps are removed. Some exposure to burrowing or ground nesting organisms near treatment furrows is possible as injections occur and gases disperse through soils.

Since the completion of the Problem Formulation, data was submitted for acute vapor phase exposure to adult honey bees, and results indicate that methyl bromide measured concentrations in the air would have to be greater than 233 ppm for over 4 hours before lethal effects are observed. There is uncertainty about chronic risks to honey bees, as lethal effects from acute

exposure were not recorded until 20 hours after the 4-hour exposure time had ended (24-hour $LD_{50} = 359$ ppm). No mortality occurred during the initial 4 hour vapor exposure.

In the recently submitted vegetative vigor study, eight species of terrestrial plants exposed to 29 ppm of methyl bromide in air tight enclosure for 4 hours were not observed to have any significant effects. Slight reductions in height (10-14%) were observed in two other species, dandelion (*Taraxacum officinale*) and soybean (*Glycine max*). However, this duration of exposure would not be expected from off target movement from field uses.

Based on an analysis in the RED assessment which used mammal inhalation data, estimated bird inhalation data, and field monitoring data, the estimated edge-of-field air concentrations of methyl bromide did not appear to indicate a potential for acute concern. Due to lack of avian inhalation data at the time a screening model was used to predict an RQ of 0.025 using mammal acute inhalation, mammal acute oral and avian acute oral data and estimated EECs. This conclusion of low risk to birds was later confirmed with actual avian inhalation data with bobwhite quail and modeling using SCREEN3³ and PERFUM⁴ in the 2011 California Tiger Salamander (CTS) endangered species litigation assessment. However, structural uses, which were assessed for the first time in the CTS assessment, indicated marginal exceedances in the acute LOCs (acute listed species LOC = 0.1) for birds (RQ = 0.11) and mammals (RQ = 0.32). It was determined that methyl bromide atmospheric concentrations would fall below the LOC at approximately 70 meters from the treated building.

Methyl bromide is intended to be a multi-target soil sterilant. It is expected that burrowing animals or beneficial soil invertebrates adjacent to or in treated fields may be affected if there is lateral transport through soils. Any non-target organisms, such as nesting birds, found inside large treated structures are expected to be exposed if not removed before fumigation. Any nontarget organisms found beside large treated structures are also expected to be exposed for short periods if emissions occur after fumigation.

While exposure to terrestrial plants and animals to residues that have volatilized from the treatment area is possible, protective measures specified on the labels (such as minimum tarp removal times to allow degradation) designed to mitigate human health risks may also contribute to reduced exposure to non-target organisms or plants present in areas outside these buffer zone areas. In general, holding times of 24 hours after structural fumigations may allow some breakdown of methyl bromide before the compound is released into the environment during ventilation.

1.4 Drinking Water Exposure from Current Uses

The following information is based on previous assessments as no new drinking water assessment will be conducted for this review. Previous estimated EDWCs cited in table 11 of the 2005 RED were 357 ug/L for acute surface water, 1.0 ug/L for cancer chronic surface water (based on PRZM EXAMS Florida Strawberry scenario), and 6.4 ug/L for groundwater (based on

³ <u>https://www.epa.gov/scram/air-quality-dispersion-modeling-screening-models</u>

⁴ https://www.exponent.com/experience/probablistic-exposure-and-risk-model-for-fumigants

USGS monitoring data for FL, CA, and HI which gave a range of 2.5 - 6.4 ug/L for 2 California wells).

Due to the volatile nature (*i.e.*, vapor pressure, Henry's Law Constant) of methyl bromide and the methods used for its agricultural applications and current mitigation parameters, the potential for this chemical to be present in surface waters that serve as sources of drinking water is expected to be very low. Likewise, although soluble in water, methyl bromide is incorporated during pre-plant applications and the potential for it to be present in ground water is considered low due to volatility. Volatility will cause methyl bromide to move upward through the soil column and potentially overcome any downward movement toward groundwater aquifers. Additionally, when tarps are used, they will restrict downward movement from rainfall necessary to move the fumigants toward ground water sources.

While many environmental factors could impact fumigant emissions from soil, such as soil type, air temperature, soil temperature and soil organic content, the potential for exposure to methyl bromide in drinking water is expected to be very low.

2.0 Problem Formulation Update

As part of the Registration Review (RR) process, a detailed EFED Problem Formulation was published to the docket for methyl bromide (DP Barcode 41020, September 20, 2013) and Docket Number EPA-HQ-OPP-2013-0269).

2.1 Previous Risk Conclusions

Inhalation of methyl bromide vapor following soil fumigation is considered the major route of exposure for terrestrial organisms. Based on an analysis in the RED assessment which used mammal inhalation data, estimated bird inhalation data, and monitoring data, the estimated edge-of-field air concentrations of methyl bromide do not appear to indicate a potential for acute concern. This was confirmed with modeling using SCREEN3 and PERFUM in the CTS endangered species litigation assessment. However, structural uses indicated slight exceedances in the acute LOCs for birds (RQ = 0.11) and mammals (RQ = 0.32).

For aquatic organisms, the RED document concluded that exposure in surface water could result from runoff with soluble methyl bromide from fumigated fields. The only aquatic LOC exceeded was the acute endangered species LOC for aquatic invertebrates based on PRZM/EXAMS modeling of methyl bromide, with the volatilization algorithm activated. However, since the RED chapter was completed, additional information about methyl bromide's residence time in water was considered. An aquatic dissipation half-life of 72 minutes (Nelly et al., 1976) indicates that the residence time of methyl bromide in water is limited. Therefore, the contribution of methyl bromide soil fumigant application to aquatic exposure and risk has been excluded from this assessment.

Table 2-1 below summarizes the previous risk conclusions for the methyl bromide from the 2005 RED and was also included in the 2013 Problem Formulation.

Birds	Mammals	Terr. Plants	Terr. Inverts	Fish	Aquatic Inverts	Aquatic Plants	Bioaccum- ulation	Persistence	Degradates of Concern
Yes- acuteYes- acutePossibleYesNoNoNoNoIn air-high Soil and water- moderateNone							None		
Yes = at least one LOC has been exceeded in previous assessments; Some small mammals (mice and rats) as well as certain soil invertebrate groups are indicated as a target species on current labels. No = LOCs have not been exceeded in previous assessments.									
Possible=	Possible= exposure expected but no terrestrial plant toxicity data available at that time								

Table 2-1. Summary of Risk Concerns Identified in Previous Methyl Bromide Assessments

Information on labeled use patterns, and the stressors of concern for methyl bromide can be found in the Problem Formulation for this DRA/DWA at the docket listed in the Preface. It should be noted that since the Problem Formulation was published in 2013, additional products have been registered and others canceled. However, application rates and label precautions on newer products are similar to previously registered products.

As indicated previously, environmental fate and ecotoxicity data that were submitted since the Problem Formulations were evaluated and results are summarized in the data summary sections 4.0 and 5.0 and below.

3.0 Use Characterization

Methyl bromide is a restricted use broad-spectrum fumigant. It is used as an outdoor pre-plant soil sterilant for agricultural crops. It is also used for indoor quarantine uses for non-residential structures, greenhouses and shipping containers. Methyl bromide's specific mode of action is currently uncertain, although its alkylating property, as well as the possibility of forming a reactive intermediate through metabolic transformation are identified as the primary hypotheses⁵. Label warnings include language stating that Methyl bromide is a neurotoxic gas that can cause severe respiratory issues, convulsions, coma, long-term harm to the nervous system or death. Methyl bromide is commonly formulated alone or with chloropicrin (trichloronitromethane) as an emulsifiable concentrate (EC), hot gas (HG), or compressed gas (CG). Pre-plant fumigation methods for methyl bromide are as an un-tarped deep shank injection, a tarped broadcast shank, a bedded shank injection, or a tarped hot gas chemigation. Maximum rates range from 75 to 400 lbs ai/acre for all methods.

Compressed gas formulation is used in structural applications (*e.g.* flour mills, rice mills, pet food processors); post-harvest treatment of commodities (*e.g.* dates, figs, raisins, walnuts); and non-food uses (*e.g.* timber for export). Labels and publications, such as the USDA/APHIS

¹ https://www.ncbi.nlm.nih.gov/pubmed/7652197

² <u>https://www.aphis.usda.gov/import_export/plants/manuals/ports/downloads/treatment.pdf</u>

(Animal Plant Health and Inspection Services) Plant Protection and Quarantine (PPQ) Treatment Manual, contain details of the application procedures for safe and effective use of methyl bromide for structural and commodity fumigation. Application procedures include specific steps and procedures for preparation, fumigation, aeration, and post-treatment actions.

Agricultural Crop Uses

Based on the most recent Agency use assessment in 2013, the average fraction treated of crops was reported to be < 2.5% for most registered crops, with a maximum of up to 45% for strawberries, 28% for tomatoes, and 4% for peppers. Application rates for methyl bromide as a soil fumigant generally ranges between 100 – 400 lbs. a.i./A. (BEAD Chemical Profile for Registration Review: Methyl bromide (053201), February 21, 2013). There are currently several special local needs registrations available for methyl bromide for soil uses with maximum application rates of 75 – 400 lbs. ai /A.

Further information on use patterns and associated crop application information for methyl bromide are provided in EFED's Problem Formulation for methyl bromide (DP Barcode 410209, September 20, 2013)⁶.

Labels restrict methyl bromide soil application methods to un-tarped deep shank injection applications (18-inch depth), tarped broadcast shank injection applications (8 inch depth), tarped bedded shank injection applications (1 inch below the adjacent furrow surface), hand held deep probe application, and hot gas broadcast chemigation applications. Labels also include several other requirements for each application method such as the consideration of minimum injection depths, minimum tarp removal times, and maximum field sizes. These requirements are listed below:

Deep Shank Injection Untarped Application:

- Minimum shank injection depth = 18 inches not cm below the ground
- Maximum field size = 40 acres (Application = 20 acres per day per one fumigation rig)

Broadcast Shank Injection Tarped Application:

- Minimum shank injection depth = 8 inches not cm below the ground
- Minimum days to remove tarp from field = 5 days after application
- Maximum field size = 100 acres (Application = 20 acres per day per one fumigation rig)

Bedded Shank Injection Tarped Application:

- Maximum shank injection depth = No deeper than deepest point of the tuck of the tarp on both sides of the bed (~1 inch below the adjacent furrow surface)
- Tarps remain over top of beds and holes in tarp are cut where planting occurs

⁶ EFED Registration Review Problem Formulation is in Docket Number EPA-HQ-OPP-2013-0269

• Maximum field size = 100 acres (Application = 20 acres per day per one fumigation rig)

Hot Gas Broadcast Tarped Application:

- Surface tube with tarped application
- Minimum days to remove tarp from field = 5 days after application
- Maximum field size = 10 acres

Structural and Container Quarantine Uses

Methyl bromide can also be used to fumigate structures for food and/or raw material commodities contained inside storage facilities. Methyl bromide is used for structural fumigation (e.g. flour mills, rice mills, pet food processors), post-harvest treatment of commodities (e.g. dates, figs, raisins, walnuts) and non-food uses (*e.g.* logs for export). For fumigation inside structures, commodities can be treated with application rates ranging from 0.5 lbs. a.i./1,000 ft³ up to 16 lbs. a.i./1,000 ft³ for treatments to tile and timber. In addition, there two commodity fumigation uses (maximum application rates of 0.5 - 3 lbs. a.i./1,000 ft³).

Procedures for Structural and Container Uses

The following steps and procedures are general description of the process for structural or container fumigation. Detailed information regarding guidance for safety and site preparation can be found in the International Cargo Cooperative Biosecurity Arrangement (ICCBA) Guide to Performing QPS Fumigations with Methyl Bromide (Published in May 2016) or the USDA/APHIS Treatment Manual referenced previously in this document.

- **Preparation**: Includes activities to seal buildings, chambers, rail cars, etc. using plastics and tape and setting up the gas lines into the target area. Warning placards go up just before fumigation.
- **Fumigation**: Is the addition and holding of the fumigant for a set time and concentration level in the space containing the commodity. This is unique to each fumigant and fumigation situation. It is dependent upon pest, commodity, and temperature. Methyl bromide is usually held for 24 hours or less and cold chain commodities are generally on the order of 4 hours. Time weighted average (TLV-TWA): average exposure level on the basis of an 8h/day, 40h/week work schedule for methyl bromide the TLV-TWA is widely accepted as 5 ppm. For short-term exposure limit (TLV-STEL): a spot exposure for a duration of 15 minutes, that cannot be repeated more than 4 times per day with at least 60 minutes between exposure periods is employed. For methyl bromide the TLV-STEL limit is widely accepted as 15 ppm. (ICCBA Guide 2016)
- Aeration: The release of the fumigant from the treated space/commodity after treatment. Since each fumigant has different chemical properties, how much will be retained/degraded through absorption and other mechanisms may vary. The physical process of how aeration is conducted and the type of space or structure which is fumigated dictate the exposure potential for workers and bystanders.
- **Post-treatment:** Removal of the seals, tubing, etc. that were put into place during the preparation phase. Clean up of the dead pests is then performed as needed when concentration levels are deemed safe. Treatments are sometimes completed in facilities

specifically designed for fumigation and which allow for enhanced throughput and more repeat operations.

4.0 Environmental Fate Summary

A full summary of the environmental fate properties, chemical physical properties and studies previously submitted and evaluated for methyl bromide can be found in the Problem Formulation (PF) for this DRA/DWA. Further information on environmental fate properties and conclusions for methyl bromide are provided in EFED's Problem Formulation(PF) for methyl bromide previously referenced above. Fate and chemical properties information are also provided in this document's appendices for quick reference purposes.

4.1 Laboratory Data

With the exception of the environmental chemistry methods and associated independent laboratory validation (ECMs/ILVs), no new environmental fate and transport studies were submitted and reviewed after the release of the PF. Two ECM studies were submitted for determination of methyl bromide and/or chloropicrin in the air, namely ECM-1: for determination of methyl bromide (MRID 495439-02) and ECM-2: for determination of methyl bromide (MRID 495439-01). The two methods were accompanied with an ILV (MRID 498035-01). The limit of quantification (LOQ) for ECM-1 is 0.1 μ g of M-Br/tube while LOQ for ECM-2 is 0.05 μ g of M-Br/tube and 0.1 μ g of chloropicrin/tube. Both ECMs were classified as supplemental.

4.2 Field Volatility Data

Additionally, the PF summarized field volatility studies covering 11 sites varied in soil texture and location (CA: two California department of pesticide regulation studies and MRID 48006001) and FL, MRID 48107601).

Based on field dissipation studies in California for tarped applications, dissipation half-lives were determined to be in the range between 4 and 11 days and appeared to vary based on the application rate but may have also varied due to weather conditions (MRIDs 00013032 and 00013173). No field dissipation studies were conducted for deep shank injection/un-tarped applications, bedded tarped application, and hot gas applications (see **Section 3** on the use characterization). It is noted that the observed field dissipation half-lives of 4 and 10 days is probably a reflection of volatility (which was not measured) rather than degradation.

4.3 Monitoring Data

The natural background concentration of methyl bromide in the oceans is in the ppb range. Monitoring data from 30 different global latitudes resulted in an average concentration of 1.2 ppb (U.S. EPA 1986). Bromide, the major degradate of methyl bromide, has been identified in USGS groundwater surveys at levels ranging from 0.015 to 0.766 mg/L. In 2001-2002 surveys USGS NAWQA detected the bromide degradate in concentrations ranging from 0.061 to 15.59 mg/L.

Monitored ambient air levels of methyl bromide are in the ppb range for agricultural communities that utilize methyl bromide as a fumigant. The highest airborne levels of methyl bromide are observed near the ground level when agricultural fields, greenhouses or buildings are actively undergoing fumigation. Measured atmospheric concentrations in California communities when fumigation was occurring had peak levels of approximately 2 to 31 ppb (California Department of Pesticide Regulation 2001). A more detailed summary of these monitored levels is presented in Table 5 of the 2005 methyl bromide RED.

4.4 Environmental Fate Conclusions

The suite of environmental fate data evaluated to date, which includes laboratory and field studies, provide evidence that volatility is the primary route of dissipation for methyl bromide.

In water methyl bromide degrades moderately by hydrolysis with half-lives ranging from 11 to 15 days in alkaline and acidic environments at 25°C. Methanol and the bromide ion were degradates detected at high levels (MRID 42720201). Methyl bromide also degrades through direct photolysis in water at similar rates as in hydrolysis with a half-life value at 9 days (Atkinson, 1989). Overall, volatilization of methyl bromide, with a dissipation half-life of 72 minutes (Nelly et al., 1976), is expected to mediate its overall decline in water.

Given its high-water solubility, leaching of dissolved methyl bromide to ground water is possible in well-drained sandy soils in areas where water table is shallow under field application scenarios, though any methyl bromide reaching surface water by drift or run-off is not expected to be persistent in water. Therefore, aquatic exposure and surface drinking water exposure are expected to be relatively insignificant. Likewise, while methyl bromide might be found in shallow ground water that serves as a drinking water source, the probability of this is considered low, as the volatility of the chemical will counteract any downward movement into the ground water.

The main dissipation process of methyl bromide for all uses is expected to be from escape to the atmosphere due to volatilization. For agricultural uses it is expected that post-application soil sealing methods (e.g., tarps or soil) will be the primary factor in controlling off-site movement of methyl bromide to the atmosphere or through the soil via diffusion.

5.0 Ecotoxicity Summary

References for the ecological effects data previously submitted for methyl bromide can be found in the Problem Formulation for this DRA. Only a brief summary is provided below.

Methyl bromide is characterized by moderate toxicity on an acute exposure basis to fish and invertebrates, with observed LC_{50} values of 3.9 mg ai/L and 2.6 mg ai/L for Rainbow trout

(*Oncorhynchus mykiss*) and *Daphnia magna*, respectively. It should be noted that the fish study required placement of test organisms in a sealed chamber in order to maintain concentrations for adequate period to obtain the lethal concentration endpoint (MRID 43066701).

For birds, two acute studies conducted with the bobwhite quail (*Colinus virginianus*) were submitted and evaluated. One study was an acute oral study and one was an acute inhalation study. Moderate toxicity was observed in the oral dose study for this species with an LD₅₀ of 73 mg ai/Kg bw (MRID 43085901) and 100 % mortality observed at 125 mg ai/Kg bw concentration level. Reduced body weight was observed at the lowest dose of 31.3 mg ai/Kg bw. In the avian inhalation study, the LD₅₀ was determined to be 561 ppm in air, with 100% mortality observed at the 788 ppm level after a 4 hour gas exposure period (MRID 48515601). Ataxia, hyperactivity and labored respiration were also observed in 258 and 505 ppm concentration levels immediately after 4 hour exposure. Moderate toxicity was observed in laboratory rat oral gavage (female LD₅₀ = 86 mg/Kg) and rat inhalation (LC₅₀ = 780 ppm = 303 mg/L in air) studies reviewed by the Agency. Results of these studies are also captured in tables in Appendix C of this document.

A previous 2011 search of open literature using the EPA ECOTOX database did not produce any relevant non-target organism data. A subsequent 2018 refresh also did not return any additional published literature pertinent for our risk assessment needs.

5.1 Ecotoxicity Data

Since the time of the publication of the PF, there were no additional aquatic data submitted in support of methyl bromide for registration review. For terrestrial organisms, data on the vapor phase exposure to adult honey bees and terrestrial plants were submitted and are summarized in **Table 5-1**.

Table 5-1. Summary of ecotoxicity studies submitted for methyl bromide since the publication of the PF.

Taxonomic Group	Study Type	Test Material (% a.i.)	Test Species	Toxicity Value (all units in terms of µg/L measured a.i.)	MRID (Classification)	Comments
Pollinator Insects	Acute	100	Honey bee, Apis mellifera	24-hr $LD_{50} = 359 \text{ ppm}$ in air	50011601 (Acceptable)	All mortality occurred after the 4 hour exposure window
Terrestrial Plants	Acute	100	4 Monocots 6 Dicots	$EC_{25} > 29$ ppm in air. NOAEC < 29 ppm for dandelion and soybean*	49171601 (Acceptable)	*10-14% height reduction after 21 days at 29 ppm. All plants survived.

*Significant inhibitions relative to the negative control (p<0.05: Dunnett's test) at 0.29, 2.8, and 29 ppm for soybean and at 29 ppm for dandelion

Adult worker honey bees (*Apis mellifera*) were exposed methyl bromide for 4 hours at nominal concentrations of 18.8, 37.5, 75.0, 150, 300 and 605 ppm (600 ppm measured) ppm. The bees exposed to 605 ppm suffered 100% mortality within the 20-hour period after exposure ended whereas the bees exposed to the 300 ppm (24-48-hour measured = 233 ppm) displayed only 2

mortalities (3.3% of treated bees). Thus, the mortality was latent, in that no bees died during the actual 4-hour exposure period. During the 48-hour observation period bees in the highest three concentrations displayed lethargy and loss of equilibrium.

A 21-day study for evaluation of potential effects to vegetative vigor to terrestrial plants from exposure to methyl bromide vapor was submitted and evaluated after the PF (MRID 49171601). Eight of the ten species of terrestrial plants exposed to 29 ppm of methyl bromide in an air tight enclosure for 4 hours were not observed to have any significant effects after a 21-day observation period. Slight, but statistically significant (p<0.05) reductions in height (10-14%) were observed for two species, dandelion (*Taraxacum officinale*) and soybean (*Glycine max*) plants. Based on these surrogate test species, adverse effects to survival and growth of non-target plants from vapor exposure are expected to be minimal if such exposure occurs.

A 21-day study on the potential effects of methyl bromide on the seedling emergence was initially requested following the PF, but subsequently waived based on an evaluation of Methyl Bromide Industry Panel (MBIP) comments regarding the deep injection requirements for orchard use. EFED agreed that the danger to potential adjacent crops may be minimal from lateral transport through soils following consultation with the Biological and Economic Analysis Division (BEAD) which indicated that the un-tarped methyl bromide use is small, and that exposure scenarios with methyl bromide translocation via runoff would be limited. In addition, EFED agrees that exposure due to diffusion alone will not likely occur over large enough distances from the treated area to impact non-target plant seeds off the treated field.

5.2 Incident Data

A November 2018 search of the Office of Pesticide Programs Incident Data System yielded no ecological incidents for methyl bromide use. It should be noted that this system is dependent on whether reports are received from registrants, states, EPA regional offices or other federal agencies. Incidents involving wildlife may not always be observed immediately after applications are made.

5.3 Ecotoxicity Conclusions

The ecotoxicity data submitted since the Problem Formulation was published for methyl bromide in 2013, provide additional evidence that this chemical is toxic to terrestrial pollinator species at exposure levels of 600 ppm in air and displays little effect to crop plants at up to 29 ppm in air. Based on actual monitored maximum levels of 0.032 ppm in high use areas of California (see Section 5.3) these air concentrations are not expected from tarped field uses or enclosed structural uses if proper mitigation procedures are followed as outlined in Section 3.1 above. Un-tarped field applications, which are not common according to Agency use analyses, require deep injection (18 inches) underground. Whether this is adequate to prevent escape from soils is an uncertainty.

Aquatic exposure to methyl bromide has not been assessed in this review because exposure to aquatic organisms is expected to be insignificant due to short residence time, as previously discussed.

For terrestrial animals, the main route of exposure to methyl bromide is expected to be via inhalation. For terrestrial plants, exposure to vapor phase methyl bromide is expected based on air monitoring detections near use areas.

In previous PERFUM modeling conducted for the California Tiger Salamander (CTS) assessment the upper 90th percentile peak (one-hour) EECs in air ranged between 1,554 – 230,769 μ g/m³ (0.4 – 59.43 ppm, converted from the ideal gas law) for structural uses of methyl bromide. For non-targeted ambient air, the highest measured concentration methyl bromide most representative of background levels was 560 ppt. Many air monitoring studies have been conducted in California to determine the concentrations of methyl bromide in air adjacent to the methyl bromide application sites associated with specific application methods. The highest methyl bromide measured concentration was 27 ppm (104,842 μ g/m³) in conjunction with structural applications and 3.35 ppm (13,008 μ g/m³) for soil applications.

Based on these predicted and monitored air concentrations and recent study submissions for acute honey bee inhalation and terrestrial plant effects from vapor exposure (LD_{50} for bees = 359 ppm; 4-hour exposure with 48-hour observation and EC₂₅ > 29 ppm for plants; 4-hour exposure with 21-day observation) levels of concern for pollinator insects or terrestrial plants are not exceeded. Based on this data, as well as previous toxicity data for birds and mammals, risk to terrestrial species is not predicted outside of the treated areas.

Further information on ecological effects, and previous ecological risk assessment conclusions for methyl bromide are provided in EFED's Problem Formulation for methyl bromide referenced earlier in this document. Ecological effects data are also summarized in this document's appendices for quick reference purposes.

6.0 Exposure Characterization

The major route of absorption of methyl bromide vapors for terrestrial organisms is through the lungs. Some of the compound is excreted through the lungs as unchanged methyl bromide, but a significant amount also undergoes metabolic decomposition. The primary breakdown product is the bromide ion, which is detectable in the blood and tissues and is excreted in the urine. Organic bromides also appear in stomach fluids and mucous (Extension Toxicology Network, EXTOXNET).

Terrestrial vertebrates, such as insectivorous birds, reptiles and mammals and beneficial invertebrates that may be on or burrowed into the treated field or immediately downwind of a treated field during and shortly after treatment are expected to be potentially exposed to methyl bromide vapors. However, the concentrations expected from current uses of methyl bromide are not expected to present exposure levels of concern for terrestrial organisms or plants outside of the immediate treated field area or structures if adequate measures such as tarps and careful sealing of structures are employed to prevent escape of vapors. Mandatory post-treatment hold times for structural and tarped applications to allow breakdown of parent residues will also reduce exposure levels.

Due to the volatile nature of methyl bromide, it is not expected to persist in surface waters that may serve as drinking water sources for wildlife. Likewise, while methyl bromide might be found in shallow ground water that serves as a drinking water source, the probability of this is considered low, as the volatility of the chemical will counteract any movement down into the ground water.

7.0 General Conclusions

7.1 Risk Conclusions Summary for Agricultural Field Uses

Based on the considerations described previously, exposure via residues in drinking water used by wildlife from the conventional uses of methyl bromide, though possible, is not expected. For reasons like those that limit exposure to human drinking water sources, exposure to aquatic organisms is also expected to be low. Terrestrial vertebrates and invertebrates that are on or burrowed under a treated field or downwind of a treated field during and immediately after treatment are expected to be at risk.

While bystander buffer zones specified on the labels are designed to mitigate human health risks, terrestrial plants and wildlife (such as burrowing owls and small mammals), or ground nesting pollinator insects (such as bumble bees), that inhabit or venture into these buffer zone areas are expected to be exposed to reduced concentrations. Though low, these concentrations may not be below the levels of concern. Mitigations designed to reduce fumigant exposure levels to humans, such as minimum holding times under tarps, may help to mitigate exposure to non-target organisms.

7.2 Risk Conclusions Summary for Closed Container and Building Uses

For use in fumigation of import/export commodities 2016 USDA/APHIS (Animal Plant Health and Inspection Services) PPQ Manual precautions include containment of vapors until reduced to 5 ppm air concentration before release from treatment chambers or enclosures. This would reduce levels well below the inhalation LD_{50} levels of 561 ppm in air for bobwhite quail, 780 ppm for laboratory rat, and 188 ppm for the laboratory mouse. Risk to terrestrial wildlife from release of vapors outside of chambers at this level is not anticipated.

Methyl bromide released from treated structures to the outdoors can be transported to groundlevel via dispersion processes such as via building downwash and wake cavities. Large treated structures include grain mills, industrial facilities, warehouses, cargo holds with fumigation chambers, and other storage facilities. Methyl bromide post treatment releases from buildings may occur through active aeration involving mechanical ventilation or passively through building leakage and opened entry ways such as windows and doors. Usage in larger buildings or greenhouses and subsequent potential for harmful exposure to non-target organisms outside these structures will be dependent on how long vapors are held within the sealed structures before release.

7.3 Overall Conclusions

Based on the empirical evidence regarding the volatility of methyl bromide, the lack of nontarget organism incidents, the low levels of methyl bromide monitored in air and water, and the stringent label restrictions for prevention of off target drift; the current methyl bromide uses are not expected to result in significant ecological risk to non-target organisms in areas adjacent to use sites. As previously discussed, aquatic habitats and organisms are not expected to be exposed from current usage. Terrestrial non-target organisms which may be unintentionally exposed within these use site areas (agricultural fields or large storage structures) are expected to be impacted due to the highly toxic nature of methyl bromide.

Appendix A: Submitted Studies and Open Literature Cited

053201 Methyl Bromide Fate Chemistry Bibliography

Hydrolysis

MRID	Citation Reference
147718	Craine, E. (1985) A Hydrolysis Study with Methyl Bromide: Project WIL-49003. Unpublished study prepared by WIL Research Laboratories,. Inc. 47 p. Submitted by Great Lake Corp. Research Report, Analytical 85:1, Jan 13, 1984.
152841	Moelwyn-Hughes, E. (1938) The hydrolysis of the methyl halides. Proc. Royal Soc., London CLXIV(A):295-306.
42720201	Lee, H. (1993a) Hydrolysis of Methyl Bromide: Lab Project Number: BR289.1:93. Unpublished study prepared by Bolsa Research Associates, Inc. 35 p.
No MRID	Lee, H. (1993c) Protocol: Hydrolysis Study of Methyl Bromide. Project No. BR 289. 1:92. Unpublished protocol Developed by Bolsa Research Associates, Inc., Hollister, CA. for the Chemical Manufacturers Association, Washington, DC.
No MRID	Lee, H. (1993d) Protocol: Hydrolysis Study of Methyl Bromide. Project No. BR 289. 1:92. Unpublished protocol Developed by Bolsa Research Associates, Inc., Hollister, CA. for the Chemical Manufacturers Association, Washington, DC.
Photolysis	
MRID	Citation reference
42720301	Lee, H. (1993b) Photohydrolysis of Methyl Bromide: Lab Project Number: BR289.1:93. Unpublished study prepared by Bolsa Research Associates, Inc. 44 p.

147719 Castro, C.; Belser, N. (1981) Photohydrolysis of methyl bromide and chloropicrin. J. Agric. Food Chem. 29(5):1005-1008. Submitted in Response to Data Call-in Notice Dated 5/16/84.

Photodegradation-air

MRID Citation Reference

45644201 Winegar, E. (2002) Methyl Bromide Ambient Air Monitoring in Oxnard/Camarillo and Santa Maria August-October, 2001. Unpublished study prepared by Applied Measurement Science. 53 p.

Aerobic soil metabolism

MRID Citation Reference

42537901 Ogle, L. (1992) Aerobic and Anaerobic Soil Metabolism of Methyl Bromide: Lab Project Number: 266-040. Unpublished study prepared by Radian Corp. 185 p.

Anaerobic soil metabolism

MRID Citation Reference

42537901 Ogle, L. (1992) Aerobic and Anaerobic Soil Metabolism of Methyl Bromide: Lab Project Number: 266-040. Unpublished study prepared by Radian Corp. 185 p.

Leach/adsorption/desorption

MRID Citation Reference

14462 Munnecke, D.E.; Kolbezen, M.J.; Stolzy, L.H. (1969) Factors affecting field fumigation of citrus soils for control of Armillaria mellea. Proceedings of the First International Citrus Symposium 3:1273-1277. (Also In unpublished submission received Jun 19, 1973 under 464-104; submitted by Dow Chemical U.S.A., Midland, Mich.; CDL:008486-E) 152098 Craine, E. (1984) Protocol: Adsorption Study with Soil and Chloropicrin. Unpublished study prepared by WIL Research Laboratories. 3 p. 152099 Craine, E. (1984) Protocol: Adsorption Study with Soil and Methyl Bromide. Unpublished study prepared by WIL Research Laboratories. 3 p. 157128 Resnis, P.; Craine, E. (1986) An Adsorption Study with Soil and Methyl Bromide: Research Report, ACC Analytical 86:6: Project WIL 49002. Unpublished study prepared by WIL Research Laboratories, 261494 Inc. 38 p. 42537802 Resnis, P.; Craine, E. (1986) An Adsorption Study with Soil and Methyl Bromide: Lab Project Number: 49002. Unpublished study prepared by WIL Research Laboratories, Inc. and BOLSA Research Associates. 48 p.

Volatility - lab

MRID Citation Reference

41644101 Craine, E. (1985) A Laboratory Volatility Study with Methyl Bromide and Chloropicrin: Lab Project Number: WIL/78001. Unpublished study prepared by Wil Research Laboratories, Inc. 35 p.

Volatility - field

MRID Citation Reference

- Ajwa, H.; Sullivan, D. (2010) Monitoring of Methyl Bromide and Chloropicrin Field Emissions from Shank Applications at Shallow and Deep Injection Depths. Project Number: HA200901. Unpublished study prepared by University of California, Davis and Sullivan Environmental Consulting. 573 p.
- 48107601 Ajwa, H.; Sullivan, D. (2010) Monitoring of Methyl Bromide and Chloropicrin Field Emissions from Shank Applications (Bedded and Broadcast) and a Methyl Bromide Hot-Gas Application under Totally Impermeable Film. Project Number: HA201001. Unpublished study prepared by University of California and Sullivan Environmental Consulting. 219 p.

Terrestrial field dissipation

MRID Citation Reference

- 13001 Dow Chemical Company (1959) Studies on the Surface Vapors of Methyl bromide Following the Application of Brozone and Liquid Methyl bromide Injected Six to Eight Inches Below the Soil Surface. (Unpublished study received Apr 23, 1964 under 464-223; CDL: 102671-A)
- 13032 Lear, B. (1972) Effect of Methyl bromide on Control of Different Nematodes. (Unpublished study including letter dated Jan 25, 1972 from B. Lear to Richard C. Storkan, received Jun 19, 1973 under 464-104; prepared by Univ. of California--Davis, Agricultural Experiment Station, Dept. of Nematology, submitted by Dow Chemical U.S.A., Midland, Mich.; CDL:008486-H)
- 14462 Munnecke, D.E.; Kolbezen, M.J.; Stolzy, L.H. (1969) Factors affecting field fumigation of citrus soils for control of *Armillaria mellea*. Proceedings of the First International Citrus Symposium

	3:1273-1277. (Also~In~unpublished submission received Jun 19, 1973 under 464-104; submitted by Dow Chemical U.S.A., Midland, Mich.; CDL:008486-E)
161982	Methyl Bromide Industry Panel (1986) [Methyl Bromide Field Dissipa- tion Study: Data Call in Notice for Ground Water-data]. Unpublished compilation. 101 p. Accession No. 264018.
43085101	Ivancovich, A. (1987) ChloropicrinField Dissipation Study: Lab Project Number: BR11:87.1. Unpublished study Prepared by Bolsa Research Associates. 144 p.
45343301	Gillis, M. (2000) Soil Dissipation of Methyl Bromide Soil Gas from a Drip Compared to a Soil Injection Application: Lab Project Number: TC364.1. Unpublished study prepared by Trical Inc. and Bolsa Research Associates, Inc. 31 p.
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152338	Dally, L. and J. Rowe (1985) California Methyl Bromide Sampling Study. Unpublished Study Received on July 26, 1985 under 57854-4. Prepared by Golden Associates and Submitted by Great Lakes Chemical Company. Study ID: Accession No. 258932.
152337	Lozier, W.B. and J. Baker (1985) Florida Methyl Bromide Sampling Study. Unpublished Study Received on July 26, 1985 under 57854-4. Prepared by Golden Associates and Submitted by Great Lakes Chemical Company. Study ID: Accession No. 258931.
258931	Lozier, W.B. 1985. Golder Associates, Inc. (1985) Florida Methyl Bromide Sampling Study: No. 853-3068; ABI No. 202-225/230/246. Unpublished study prepared in cooperation with Applied

Aquatic Field Dissipation

MRID Citation Reference

Biology, Inc. 37 p.

No MRID Pickrell, S., S. Dwinell and D. Tterlikkis (1985) Chemical Residues in Freshwater Resulting from Soil Fumigation by Methyl Bromide and Chloropicrin. Report PRS 85-01. Unpublished Study Prepared and Submitted by the Pesticide Review Section, State of Florida Department of Environmental Regulation, Tallahassee, FL.

Non-Guideline Fate and Chemistry Selections

MRID Citation Reference

- 118834 Kolbezen, M.; Munnecke, D.; Wilbur, W.; et al. (1974) Factors that affect deep penetration of field soils by methyl bromide. Hilgardia 42(14):465-492. (Also In unpublished submission received Jun 30, 1975 under 5785-41; submitted by Great Lakes Chemical Corp., West Lafayette, IN; CDL:220944-A)
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- 48121505 Siemer, S. (1992) Non-Tarped Shallow Shank and Deep Shank Injection Protocol for Measurement of Methyl Bromide Drift Offsite. Project Number: 924096E. Unpublished study prepared by Siemer & Associates. 38 p.

48121506	Siemer, S. (1992) Tarp-Bed and Tarp-Shallow Fumigation Protocol for Measurement of Methyl Bromide Drift Offsite Including Application and Tarp Removal or Venting as Separate Source Times for Methyl Bromide Release. Project Number: 924096F. Unpublished study prepared by Siemer & Associates. 39 p.
13175	Voth, V., D.E. Munnecke, A.O. Paulus, et al. (1971) Effect of Tarp Thickness and Dosage on Response to California Strawberries to Fumigation. Unpublished Study Received Oct 3, 1973 under 5785-EX-26, Submitted by Great Lake Chemical Corp., West Lafayette, IN. CDL: 210143-E.
40863301	Ogle, Larry D. (1988) Final Report for the Environmental Fate Studies of Methyl Bromide. Performed by Radian Corporation for the Methyl Bromide Industry Panel. Received by EPA on October 25, 1988. MRID #; 40863301.
40863301	Ogle, Larry D. (1988) Final Report for the Environmental Fate Studies of Methyl Bromide. Performed by Radian Corporation for the Methyl Bromide Industry Panel. Received by EPA on October 25, 1988. MRID #; 40863301.

No MRID Moelwyn-Hughes, E. 1931. Kinetics of reactions in solution. Part 1

Methyl Bromide Eco-Effects Bibliography

Avian Single Dose Oral Toxicity

MRID Citation Reference

- 10248 Hudson, R.H. (1972) Potassium azide: Internal Report Series in Pharmacology. (Unpublished study including letter dated Sep 18, 1972 from R.H. Hudson to Warren H. Zick, received on unknown date under 3F1358; prepared by U.S. Fish and Wildlife Service, Denver Wildlife Research Center, Section of Pesticide-Wildlife Ecology, submitted by PPG Industries, Inc., Chemical Div., Pittsburgh, Pa.; CDL:093627-C)
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MRID Citation Reference

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Acute Toxicity to Freshwater Fish

MRID Citation Reference

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- 43066701 Drottar, J.; Swigert, K. (1993) Methyl Bromide: A 96-Hour Static Acute Toxicity Test with the Rainbow Trout (Oncorhynchus mykiss): Final Report: Lab Project Number: 264A-105A. Unpublished study prepared by Wildlife International Ltd. 41 p.

Acute Toxicity to Freshwater Invertebrates

MRID Citation Reference

- 42932901 Drottar, K.; Swigert, J. (1993) Methyl Bromide: A 48-Hour Static Acute Toxicity Test with the Cladoceran (Daphnia magna): Final Report: Lab Project Number: 264A-102B. Unpublished study prepared by Wildlife International Ltd. 41 p.
- 42934001 Rosica, K. (1993) Letter Sent to R. Douglas dated September 15, 1993: Preliminary results of an invertebrate toxicity study with daphnia magna. Prepared by Methyl bromide Industry Panel. 3 p.

Acute Toxicity to Pollinators

MRID Citation Reference

50011601 Porch, J., Weinberg J., and Krueger, H. 2016. Methyl Bromide: An Acute Vapor Exposure Toxicity Study with the Honey Bee. EAG Laboratories

Toxicity To Terrestrial Plants

MRID Citation Reference

49171601 Weinberg, J.T. 2013. A Toxicity Test to Determine the Effects of Methyl Bromide (MeBr) on the Vegetative Vigor of Ten Plant Species. Unpublished study performed by WIL Research and Ashland University, Ashland, Ohio, and AGVISE Laboratories, Inc., Northwood, ND. Laboratory Project ID: WIL-49018.

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Appendix B. Methyl bromide Summary of Fate and Chemical Characteristics

Property	Value and units	MRID or Source	
Structure	H	EPISUITE	
Chemical Formula	CH ₃ Br	Tomlin, 1994	
Molecular Weight	94.94 g/mol	Tomlin, 1994	
Vapor pressure (25°C)	1,620 torr	Tomlin, 1994	
Henry's Law Constant	$7.34 \text{ x } 10^{-3} \text{ atm} \cdot \text{m}^3/\text{mol}$	Yates and Gan, 1998	
Water Solubility (25°C)	15,200 mg/L	Horvath, 1982	
Octanol – water partition coefficient (log K _{OW})	1.18	EPISUITE	
Half-life in air (troposphere) (days)	210 days	Atkinson, 1989	

Table B-1. Physical and chemical properties of methyl bromide.

Table B-1 lists the environmental fate properties of methyl bromide. Detailed information on the degradates is presented in **Table B-2**. The open literature has been used to fulfill many outstanding data gaps related to the environmental fate. Details describing evidence for the behavior of methyl bromide in the environment is described below.

Table B-2. Summary of methyl bromide environmental fate propertie

Study	Value and unit	Major Degradates ^{4,6}	MRID # or Citation	Study Classification, Comment
Abiotic Hydrolysis	$\frac{\text{MRID } 42720201}{\text{t}_{\frac{1}{2}} = 11 \text{ days (pH 5, 25°C)}}$ $t_{\frac{1}{2}} = 11 \text{ days (pH 7, 25°C)}$ $t_{\frac{1}{2}} = 15 \text{ days (pH 9, 25°C)}$ $\frac{\text{Papiernik et al., 2000}}{\text{t}_{\frac{1}{2}} = 20 \text{ days (pH 7, 25°C)}}$	Bromide ion (pH 5, 7, and 9) and Methanol (pH 5, 7, and 9)	42720201 Papiernik et al., 2000	Supplemental
Aqueous Photolysis	$t_{\frac{1}{2}} = 9$ days	Bromide Ion and Methanol	Atkinson, 1989	-
Soil Photolysis	No Data	-	NA	NA
Atmospheric Degradation	Atkinson, 1989 $t_{1/2} = 210$ days or 0.58 years(troposphere)Butler and Rodriguez, 1996Lifetime = 35 years (stratosphere)WMO, 2002Lifetime = 255.68 days or 0.7 years	Bromide Ion	Atkinson, 1989 Butler and Rodriguez, 1996 WMO, 2002	NA

Study	Value and unit	Major Degradates ^{4,6}	MRID # or Citation	Study Classification, Comment
	(total atmosphere)			
Aerobic Soil Metabolism	(total atmosphere) MRID 40863301 Bi-phasic Half Lives 1^{rst} $t_{1/2} = 1.5$ days (SL) 2^{nd} $t_{1/2} = 20$ days (SL) 1^{rst} $t_{1/2} = 0.15$ days (CL) 2^{nd} $t_{1/2} = 19$ days (CL) Papiernik et al., 2000 $t_{1/2} = 39$ days (SL, 0.92% OM) $t_{1/2} = 39$ days (SL, 0.92% OM) $t_{1/2} = 4$ days (CL, 2.51% OM) Gan and Yates, 1996 $t_{1/2} = 22$ days (SL, 0.92 % OM) $t_{1/2} = 6$ days (LS, 2.51% OM) $t_{1/2} = 6$ days (CL, 2.99% OM) $t_{1/2} = 6$ days (CL, 2.99% OM) $t_{1/2} = 6$ days (SL – moist, 0.92% OM) $t_{1/2} = 34$ days (SL – moist, 0.65 % OM) $Gan et al., 1994$ $t_{1/2} = 34$ days (SL – moist, 0.65 % OM) $t_{1/2} = 57$ days (LS – moist, 0.22% OM) $t_{1/2} = 13$ days (SL – air dry, 0.92% OM) $t_{1/2} = 39$ days (LS – air dry, 0.65% OM) $t_{1/2} = 39$ days (LS – air dry, 0.22% OM) $t_{1/2} = 6$ days (CL – air dry, 2.99% OM) $t_{1/2} = 6$ days (CL – air d	Bromide Ion and Methanol	Citation 40863301 Papiernik et al., 2000 Gan and Yates, 1996 Gan et al., 1994	Classification, Comment
	$t_{1/2} = 36$ days (SL – oven dry, 0.92% OM) $t_{1/2} = 59$ days (SL – oven dry, 0.65% OM) $t_{1/2} = 27$ days (LS – oven dry, 0.22% OM) $t_{1/2} = 47$ days (CL – oven dry, 2.99% OM)			
Anaerobic Soil Metabolism	$\label{eq:mrst} \begin{array}{l} \underline{\text{MRID } 40863301} \\ \text{Bi-phasic Half Lives} \\ 1^{\text{rst}} t_{1/2} = 6 \text{ days (SL)} \\ 2^{\text{nd}} t_{1/2} = 24 \text{ days (SL)} \end{array}$	Bromide Ion and Methanol	40863301	Supplemental

Study	Value and unit	Major Degradates ^{4,6}	MRID # or Citation	Study Classification, Comment
	$1^{rst} t_{1/2} = 2 \text{ days (CL)}$ $2^{nd} t_{1/2} = 20 \text{ days (CL)}$			
Aerobic Aquatic Metabolism	5 days (freshwater) 36 days (estuary water) 82 days (coastal seawater) 298 days (hypersaline water)	-	Goodwin et al., 1998	NA
Anaerobic Aquatic Metabolism	No Data	-	NA	NA
Mobility, unaged leaching, adsorption/ desorption and aged leaching soil column	$\begin{split} K_{oc} &= 7.07 \text{ mL/g (LS)} \\ K_{oc} &= 32.01 \text{ mL/g (LS)} \\ K_{oc} &= 17.40 \text{ mL/g (L)} \\ K_{oc} &= 16.38 \text{ mL/g (PC)} \end{split}$	-	Daelmans and Siebering, 1977	NA
Volatility from Soil (Laboratory)	No Data	-	NA	NA
Volatility from Soil (Field)	See Table 6 for field volatility study descriptions and volatile flux measurements	-	48107601 48006001	Pending Supplemental
Volatility from Water (Laboratory)	$t_{1/2} = 72$ minutes	-	Nelly, W.B., 1976	NA
Terrestrial Field Dissipation	St. Helena, CA Loamy Sand (MRID No. 00013032) $t_{\frac{1}{12}} = 4 - 6$ days (broadcast tarp at 300 lbs. a.i./A removed after 6 days) $t_{\frac{1}{12}} = 11 - 38$ days (broadcast tarp at 800 lbs. a.i./A removed after 6 days) Arvin, CA Sandy Loam (MRID No. 00013173) $t_{\frac{1}{12}} = 7.98$ days (broadcast tarp at 161.71 lbs. a.i./A removed after 11 days) Lodi, CA Sandy Loam (MRID No. 0013173) $t_{\frac{1}{12}} = 7.98$ days – 9.75 days (broadcast tarp between 121.28 - 161.71 lbs. a.i./A removed after 11 days)	-	00013032 00013173	Supplemental Supplemental

Study	Value and unit	Major Degradates ^{4,6}	MRID # or Citation	Study Classification, Comment
Bio-concentration Factor (BCF) - Species Name	No Data ²	-	NA	NA

¹ Legend for Soil Types: SL = Sandy Loam

LS = Loamy SandL = Loam PC = Peaty Clay NPM= Nursery Potting Mix

NPM= Nursery Potting Mix CL = Clay Loam
² Methyl bromide's Log Kow < 3. Therefore, no data are necessary.
³ All studies used methyl bromide as the test substance.
⁴ Dashes mean no constituents found or measured.
⁵ NA means not applicable.
⁶ Degradate levels not quantified in studies.

Appendix C Ecotoxicity Data Summary

Taxonomic Group	Study Type	Surrogate Species	Toxicity Values (ppm)	Acute Toxicity Classification	Source
Freshwater fish ¹	Acute	Rainbow trout, Oncorhynchus mykiss	$LC_{50} = 3.9$	Moderately toxic	MRID 43066701
	Chronic	Guppy, Poecilla reticulata	21 D LOEC < 1.0 (100 % mortality)		Open literature Canton, 1983
Freshwater invertebrates	Acute	Water flea Daphnia magna	$\begin{array}{l} 48 \ hr \ EC_{50} = 2.6 \\ 24 \ hr \ EC_{50} = 5.3 \end{array}$	Moderately toxic	MRID 42932901
	Chronic	No data			
Aquatic Algae	Acute	Scenedesmus quadricauda	48 hr EC ₅₀ =2.2		Open literature Canton 1980
Data for acute or chronic toxicity to estuarine/marine fish, estuarine/marine invertebrates, or vascular aquatic plants have not been submitted.					

Summary Endpoints from Aquatic Toxicity Studies for Methyl Bromide.

¹Freshwater fish may be surrogates for aquatic-phase amphibians.

Summary of the Most Sensitive Endpoints from Terrestrial Toxicity Studies for Methyl Bromide.

Taxonomic Group	Study Type	Surrogate Species	Toxicity Value	Acute Toxicity Classification	Source
Birds ¹	Acute oral	Bobwhite quail (Colinus virginianus)	$LD_{50} = 73.2 \text{ mg}$ ai/kg of BW	Moderately toxic	MRID 43085901
	Acute Inhalation ²	Bobwhite quail (<i>Colinus</i> <i>virginianus</i>)	$LD_{50}=561$ ppm in air 100% mortality at 788 ppm		MRID 48515601
	Sub-acute dietary	No data			
	Chronic reproduction	No data			
Mammals	Acute Oral	Laboratory rat (<i>Rattus</i> norvegicus)	$LD_{50} = 120-160$ mg/kg (males) $LD_{50} = 86$ mg/kg (females)	Moderately toxic	MRID 43510301
	Acute Inhalation	Laboratory rat (<i>Rattus</i> norvegicus)	$LC_{50} = 780$ ppm, 4 hr exposure	HED - Category IV	Kato et al. (1986) open literature
	Chronic ³	Laboratory rat (<i>Rattus</i> norvegicus)	Reproduction NOAEL= 3 ppm LOAEL =30 ppm Weight Reduction NOEL = 30 ppm (11 week exposure)		MRID 00160477
	Inhalation	Mouse (<i>Mus</i> musculus)	6 hr LC ₅₀ =188 ppm		MRID 42504101

Taxonomic Group	Study Type	Surrogate Species	Toxicity Value	Acute Toxicity Classification	Source
Terrestrial Invertebrates	Acute contact: 4-hour vapor exposure – 48 hour observation period	Honey bee (Apis mellifera L.)	LD_{50} =359 ppm in air ⁴	Acceptable	MRID 50011601
Terrestrial plants	Vegetative vigor: 4- hour vapor exposure - 21-day observation period	Dicot (multiple species)	EC ₂₅ > 29 ppm in air	Acceptable	MRID 49171601
		Monocot (multiple species)	EC ₂₅ > 29 ppm in air	Acceptable	MRID 49171601

BW: body weight

¹Birds represent surrogates for terrestrial-phase amphibians and reptiles.

 2 Avian Acute Inhalation Study: sublethal effects, as well as delayed mortality, were reported in the treatment concentrations during and after the 4 hour exposure. Ataxia, hyperactivity and partial closure of the eyes was reported during the study for all treatment concentrations. Twitching and excessive head shaking was also reported in the 788 ppm treatment concentration (the highest concentration tested).

³ Rat: NOAEL for reproductive toxicity of 3 ppm (2.8 mg/kg/day) and a LOAEL of 30 ppm (24 mg/kg/day) based on reduced pregnancy rates (F2b generation).³Rat: NOAEL for reproductive toxicity of 3 ppm (2.8 mg/kg/day) and a LOAEL of 30 ppm (24 mg/kg/day) based on reduced pregnancy rates (F2b generation). 11-week NOAEL for parental/systemic toxicity of 30 ppm (24 mg/kg/day) and a LOAEL of 90 ppm (73 mg/kg/day) based on reduced body weight during gestation

⁴ No mortality was reported during initial 4 hour exposure. 100% adult bee mortality observed at 600 ppm and 2 % mortality at 233 ppm (measured) at 24 and 48 hours.

Uses	Formulation ¹	Applicable Statute for Use Allowance ²	Application Methods	Methyl Bromide Maximum Single Application* Rate (lb a.i./A) ⁴
Orchard Replant	EC, CG	CUE	• Deep Shank Injection Untarped (EC and CG)	300
Peppers	EC, CG	CUE		200
Peppers	EC, CG	Stockpile (CA Only)		330
Eggplant	EC, CG	CUE	Broadcast Shank Injection	350
Cucurbits	EC, CG	CUE	(EC and CG)	250
Forestry Nursery	EC, CG	CUE and QPS	Bedded Shank Injection	400
Nursery and Ornamentals	EC, CG	CUE and QPS	Tarped (EC and CG)	400
Strawberries (Eastern US)	EC, CG	CUE		240
Strawberries (CA)	EC, CG	CUE		175
Sweet Potatoes	EC, CG	CUE		350
Tomatoes	EC, CG	CUE	Broadcast Shank Injection Tarned	240
Tomatoes	EC, CG	Stockpile (CA Only)	(EC and CG)	220
Onions	EC, CG	Stockpile (GA Only)	• Bedded Shank Injection Tarped	350
Caneberries	EC, CG	Stockpile	(EC and CG)	200
Ginger	EC, CG	Stockpile (Hawaii Only)		400
Watermelon	EC, CG	SLN (CA)		200
Pepper	EC, CG	SLN (CA)		400
Forestry Nursery	EC, CG, HG	CUE	Broadcast Shank Injection Tarped	400
Nursery and Ornamentals	EC, CG, HG	CUE	(EC and CG)	400
Golf Courses and Athletic Fields	EC, CG, HG	Stockpile and QPS	• Bedded Shank Injection Tarped (EC and CG)	400
Golf Courses	EC, CG, HG	SLN (FL)	• Hot Gas Tarped Chemigation (HG only)	75

Appendix D Methyl bromide soil fumigant use information based on labels

* Only One Application Per Year is Permitted for Outdoor Uses

¹Formulation codes: EC - Emulsifiable Concentrate; HG – Hot Gas; CG – Compressed Gas ² Statute Designation Codes: CUE – Critical Use Exemption, QPS – Quarantine Pre-Shipment Exemption, SLN – Special Local Needs

³NA – Not Applicable

⁴Values represent maximum application rates on the labels. These rates are not adjusted for the area treated for application methods such as bedded tarped shank injection.