Appendix D – Evaluation of Methyl Bromide Aquatic Exposure

EFED quantitatively evaluated the potential risks to aquatic organisms in order to support the problem formulation of this risk assessment. The exposure assessment was based on the latest labeled soil fumigant uses of methyl bromide. Application methods identified included untarped deep shank injection, tarped broadcast shank injection, and bedded tarped shank injection.

Exposure estimates (presented for each application method below) were compared to the level of concern concentration based on endpoints from existing acute methyl bromide aquatic toxicity studies[1]. The most sensitive endpoint, from the aquatic invertebrate (*daphnia*) study LC_{50} of 2,600 μg/L (LOC concentration of 130 μg/L or concentration level which exceeds the acute endangered species LOC) was ultimately used for the basis of this comparison. Another aquatic toxicological study included the freshwater fish study (*rainbow trout*) where an LC_{50} value of 3,900 μg/L was observed. The underlying uncertainty that exists with this analysis is that there are several aquatic toxicity studies that have not been conducted for methyl bromide. These include the following studies:

- Oyster Acute Toxicity Test (shell deposition) (850.1025)
- Mysid Acute Toxicity Test (850.1035)
- Aquatic Plant Growth Toxicity (Tier II) (850.4400)

Therefore, this evaluation for risk potential from methyl bromide aquatic does not consider these receptors. However, the toxicity of methyl bromide is not expected to vary greatly from the available existing rainbow trout and daphnia studies.

<u>Untarped Deep Shank Injection and Tarped Shank Injection Applications</u>

Methyl bromide aquatic exposure for untarped deep shank injection and tarped shank injection applications was estimated using the PRZM/EXAMS model Georgia Farm Pond scenario including the use of the volatility algorithm. Details of the modeling inputs including the description and justification of fate, physical chemical, crop management parameters are included in Attachment 1 of this document, and the result output files are shown in Attachment 2. **Table D-1** shows the surface water peak EECs for the crop scenarios modeled consistent with the information provided by PRD. **In general, no exceedences with the Acute Endangered Species LOC are noted.** The highest upper-bound EEC occurred for tarped shank injection applications in the Florida Pepper scenario which is roughly 73 percent of the LOC concentration of 130 μg/L. The modeling results for tarped shank injection application **do not** account for shielding of precipitation elements due to the tarp, and is therefore conservative.

[1] The acute endangered species level of concern of 0.05 x LC_{50} was considered as a benchmark for potential risk.

Table D-1. PRZM/EXAMS 1-in-10 year upper-bound peak EECs in surface water for untarped deep shank injection and tarped shank injection methyl bromide applications.

Crop Grouping	PRZM/EXAMS Crop Scenario	Application Rate (lbs. a.i./A)	1-in-10 Year Peak EECs (μg/L)
Untarped Deep Shank Injection Methyl Bromide Application			
Orchard Replant	CA Almonds	400	8.64
	CA Grape	400	0.09
	OR Apple	400	11.8
	GA Pecans	400	0.01
Tarped Broacast Shank Injection Methyl Bromide Application			
Peppers and Eggplant	CA Pepper	396	2.21
	FL Pepper	**300**	**94.1**
Cucurbits	FL Cucumber	240	44.8
Forestry Nursery	OR Xmas Tree	400	3.2
Nursery and Ornamentals	CA Nursery	400	0.32
	MI Nursery	400	21.2
Strawberry Fruit	CA Strawberry*	288	0.19
	FL Strawberry	288	81.7
Sweet Potatoes	CA Potato*	400	0.08
Tomatoes	CA Tomato	264	1.47
Onions	GA Onion	390	77.7
Golf Courses and Turf	CA Turf	400	0.02
	FL Turf	400	25.2

* PRZM/EXAMS crop scenarios developed especially for the California Red-Legged Frog risk assessments. Maximum EEC shown in bold.

Bedded Tarped Shank Injection Applications

Estimating exposure for bedded tarped scenarios is difficult given the uncertainties with the mass transfer of methyl bromide through the tarp versus leakage around the tarp and into the furrow adjacent to the bed. In addition, there are various uncertainties that exist in environmental fate data submitted for methyl bromide including wide ranges in aerobic soil half-lives, large quantities of unaccounted mass in many of the soil volatility studies specifically to bedded tarped applications, and limited data submitted as well as highly variable half lives from open literature studies pertaining to its degradation in water. However, a peer-reviewed study in the open literature measured a dissipation half-life of 72 minutes for methyl bromide at 25 degrees Celsius in water (Nelly, W.B., 1976). With this half-life, it was determined that 12.17 percent or greater of the applied would need to enter the water body in order for there to be a daily average estimated exposure concentration in the Georgia Farm Pond (area = 1 ha, 2 m depth) exceeding the acute endangered species LOC concentration of 130 μg/L (based on the most sensitive endpoint from the daphnia study) given the maximum crop treated equivalent application rate of 200 lbs. a.i./A.[2]

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[2] Determined by developing a time series of hourly concentrations based upon first-order dissipation from an initial GA farm pond concentration, assuming equal mixing of dissolved methy bromide within the water body. The initial concentration was calculated according to the following equation:

$$\text{EEC} = \frac{\text{ApplicaionRate (lbs./A)} \times \frac{1.123\,\text{(kg/ha)}}{\text{(lb/A)}} \times \frac{10^{9}\,\mu\text{g}}{\text{kg}}}{\frac{10^{4}\,\text{m}^{2}}{\text{ha}} \times 2\,\text{m depth} \times \frac{1{,}000\,\text{L}}{\text{m}^{3}}}$$

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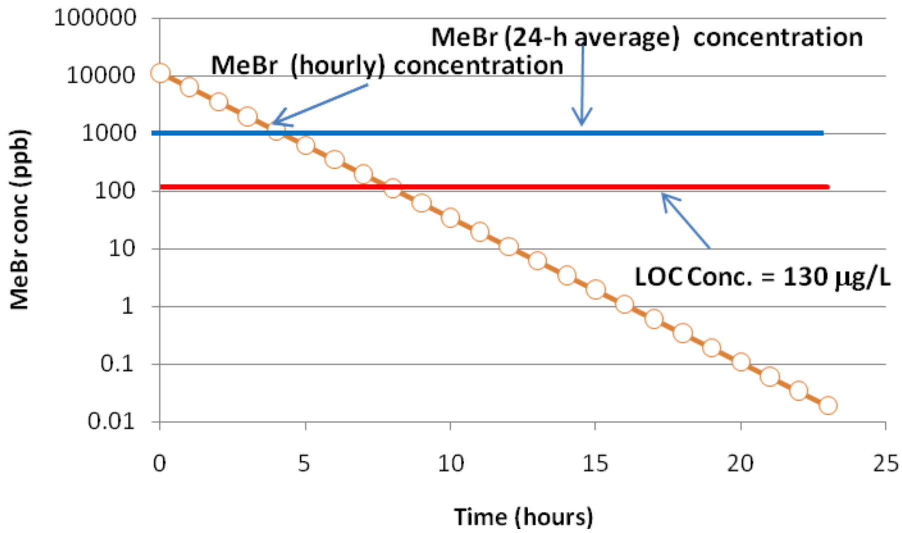
Although this is a small portion of the applied amount, two additional factors are considered:

1. Even if the total (or 100 percent of the) applied mass of methyl bromide (200 lbs. a.i./A maximum field treated application rate for methyl bromide bedded tarped applications) were somehow dissolved into the pond instantaneously during the application, it would take about 8 hours before the hourly estimated concentration would no longer exceed the LOC concentration. Although the estimated daily concentration would exceed the LOC concentration by a wide margin, that would occur largely due to a high skewness to the estimated hourly concentrations early in the event. This is illustrated in **Figure D-1** below.

Figure D-1. Hourly time series for Georgia Farm Pond concentration resulting from instantaneous release of total applied methyl bromide from bedded tarped applications (200 lbs. a.i./A).



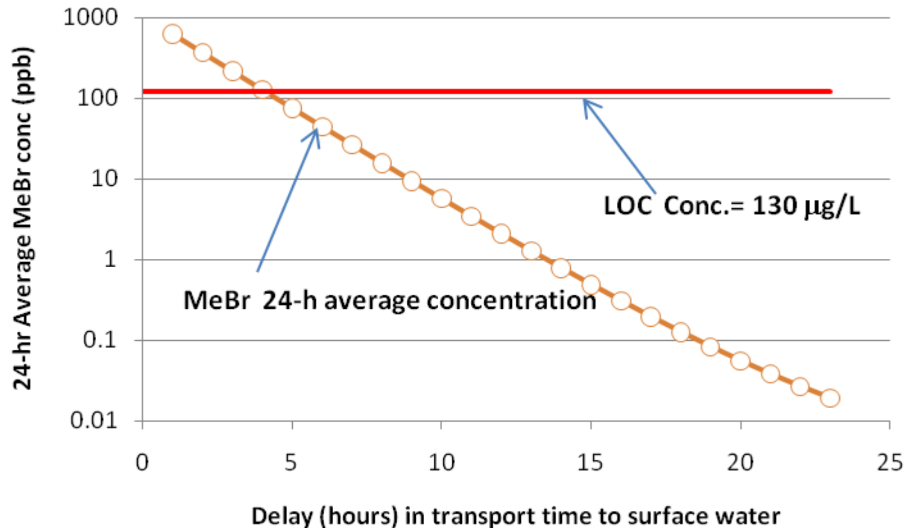
* Time series of hourly concentrations based upon first-order dissipation (72-minute volatilization half-life) from an initial GA farm pond concentration, assuming equal mixing of dissolved methyl bromide within the water body. The initial concentration was calculated according to the following equation:

$$EEC = \frac{\text{ApplicaionRate (lbs./A)} \times \frac{1.123\,\text{(kg/ha)}}{\text{(lb/A)}} \times \frac{10^9\,\mu\text{g}}{\text{kg}}}{\frac{10^4\,\text{m}^2}{\text{ha}} \times 2\text{m depth} \times \frac{1{,}000\,\text{L}}{\text{m}^3}}.$$

2. The probability that 12 percent or greater of the applied methyl bromide would be received in a water body is low. This is due to the following factors:

    a.) The rapid dissipation that is expected to occur in runoff water as indicated by the 72 minute dissipation half-life. The effect on the delay in transport time to the water body in the daily water body estimated concentration is shown in **Figure D-2** below. The LOC is no longer exceeded after 4 hours of transport time assuming all 200 lbs. a.i./A of methyl bromide is dissolved into the farm pond.

Figure D-2. Methyl bromide 24-hour average concentrations based on the delayed release of methyl bromide into the Georgia Farm Pond concentration resulting from the total applied methyl bromide being available to translocation (runoff and leaching) from bedded tarped applications (200 lbs. a.i./A).

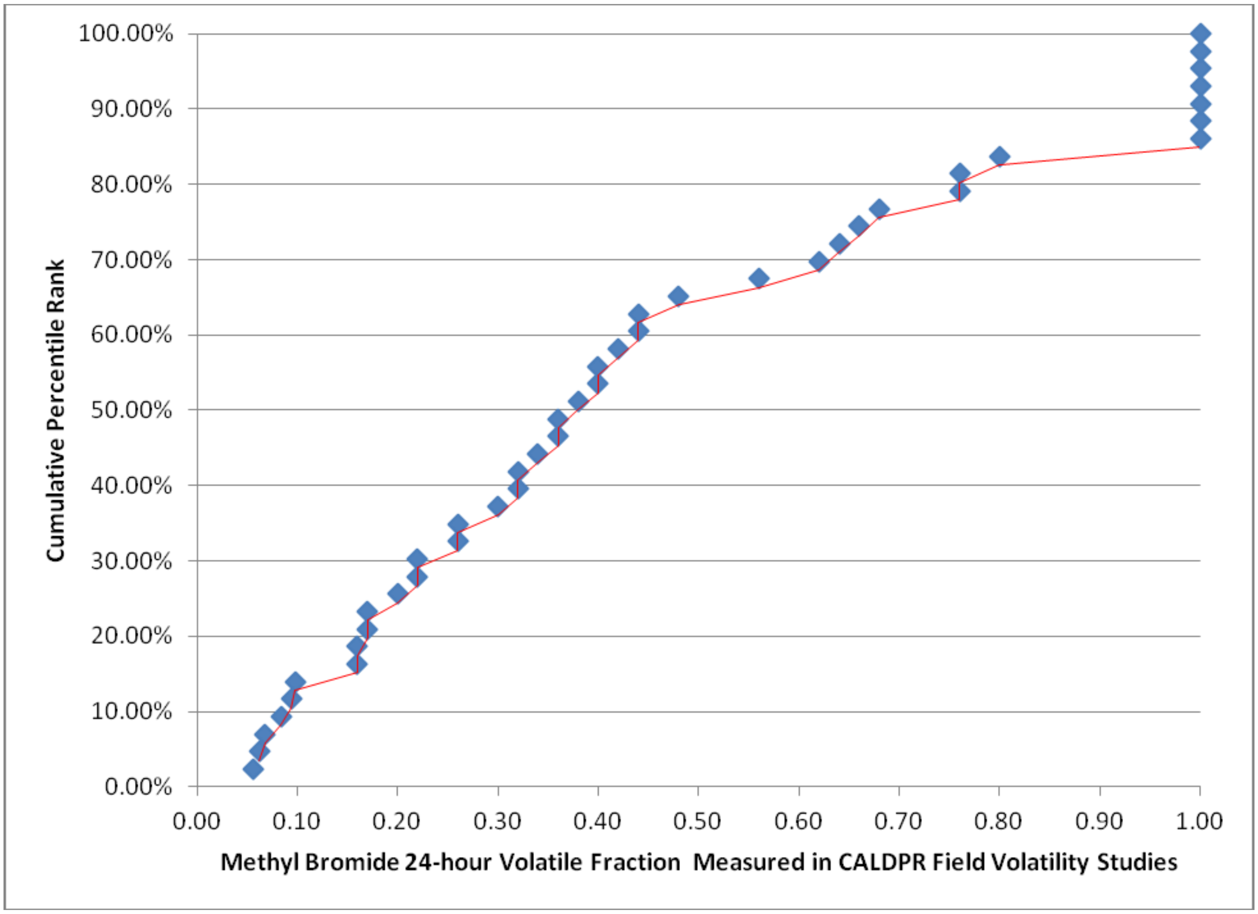


* 24-hour average concentrations developed from time series of hourly concentrations based upon first-order dissipation (72-minute volatilization half-life) from an initial GA farm pond concentration, assuming equal mixing of dissolved methyl bromide within the water body. The initial concentration was calculated according to the following equation:

$$EEC = \frac{\text{Applicaion Rate (lbs./A)} \times \frac{1.123\,\text{(kg/ha)}}{\text{(lb/A)}} \times \frac{10^9\,\mu\text{g}}{\text{kg}}}{\frac{10^4\,\text{m}^2}{\text{ha}} \times 2\text{m depth} \times \frac{1{,}000\,\text{L}}{\text{m}^3}}$$.

b.) Although highly variable in terms of volatile mass fraction, methyl bromide flux from soil has been measured in large quantities in all cases. Figure D-3 shows two distinct clustering regions of 24-hour volatile fraction measurements between 0.2 – 0.5 and at 1.0. Application methods such as tarps certainly attenuated the flux of methyl bromide in some of these studies. However, even with the tarps, some loss of methyl bromide from soil was measured.

Figure D-3. Cumulative percentile distribution for methyl bromide flux measured in CALDPR's sponsored field volatility studies.



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Attachment D-1 – PRZM/EXAMS Modeling Inputs

Table D-1-1. Summary of PRZM/EXAMS physical chemical properties and environmental fate input used for aquatic exposure estimation for methyl bromide.

PRZM/EXAMS Input Parameter	Input Value and Unit	Source
Molecular Weight	94.94 g/mol	Tomlin, 1994
Hydrolysis ($t_{1/2}$)	11 days at pH 7	MRID 42720201
Aerobic soil metabolism ($t_{1/2}$)	22 days	Upper 90th percentile bound of 6 values from Papiernik et al., 2000 and Yates, 1997
Aerobic aquatic metabolism ($t_{1/2}$)	15 days	Calculated from Goodwin et al., 1998 and EFED Input Parameter Guidance for One Study (5 days x 3)
Anaerobic aquatic metabolism ($t_{1/2}$)	Stable	Conservative Assumption
Vapor Pressure at 25 ºC	1,620 torr	Daubert and Danner, 1989
Solubility in Water at 25ºC	15,200 mg/L	Tomlin, 1994
Soil-Water Partition Coefficient (K_d)	18.0 mL/g	Mean of 4 values from Daelemans and Siebering, 1977
Henry's Law Constant	0.007 atm·m^3/mol	Yates and Gan, 1998
Enthalpy of Vaporization	5.49 kcal/mol	Chickos and Acree, 2003
Vapor Phase Diffusion Coefficient	6,944 cm^2/day	Fuller et al., 1966
Aqueous Photolysis ($t_{1/2}$)	9.0 days	MRID 42720301

Table D-1-2. Summary of PRZM/EXAMS crop management input parameter values used for aquatic exposure estimation for methyl bromide.

Crop Grouping	PRZM/EXAMS Crop Scenario	Application Rate and Intervals (lbs. a.i./A)	Application Date	Chemical Application Method (CAM) and Incoporation Depth (cm)	Application Efficiency	Spray Drift Fraction
Untarped Deep Shank Injection Methyl Bromide Application						
Orchard Replant	CA Almonds	400 (1 application)	Nov. 15	CAM = 8[1] 45.72 cm	1.0	0
	CA Grape	400 (1 application)	Apr. 1			
	OR Apple	400 (1 application)	Dec. 5			
	GA Pecans	400 (1 application)	Jun. 15			
Tarped Broacast Shank Injection Methyl Bromide Application						
Peppers and Eggplant	CA Pepper	396 (1 application)	Feb. 10	CAM = 8[1] 20.32 cm	1.0	0
	FL Pepper	300 (1 application)	Aug. 10			
Cucurbits	FL Cucumber	240 (1 application)	Apr. 25			
Forestry Nursery	OR Xmas Tree	400 (1 application)	Mar. 10			
Nursery and Ornamentals	CA Nursery	400 (1 application)	Aug. 15			
	MI Nursery	400 (1 application)	Mar. 10			
Strawberry Fruit	CA Strawberry*	288 (1 application)	Aug. 10			
	FL Strawberry	288 (1 application)	Aug. 10			
Sweet Potatoes	CA Potato*	400 (1 application)	Sept. 10			
Tomatoes	CA Tomato	264 (1 application)	Feb. 10			
Onions	GA Onion	390 (1 application)	Sept. 5			
Golf Courses and Turf	CA Turf	400 (1 application)	Feb. 10			
	FL Turf	400 (1 application)	Oct. 10			

* PRZM/EXAMS crop scenarios developed especially for the California Red-Legged Frog risk assessments.

[1] CAM = 8 =>Soil applied, entirely at incorporation depth.

Attachment D-2 – PRZM/EXAMS Modeling Output Files

Crop Grouping	PRZM/EXAMS Crop Scenario	Output File
Untarped Deep Shank Injection Methyl Bromide Application		
Orchard Replant	CA Almonds	Mb_caal.out
	CA Grape	Mb_cagr.out
	OR Apple	Mb_orap.out
	GA Pecans	Mb_gape.out
Tarped Broacast Shank Injection Methyl Bromide Application		
Peppers and Eggplant	CA Pepper	Mb_cape.out
	FL Pepper	Mb_flpe.out
Cucurbits	FL Cucumber	Mb_flcu.out
Forestry Nursery	OR Xmas Tree	Mb_ortr.out
Nursery and Ornamentals	CA Nursery	Mb_canu.out
	MI Nursery	Mb_minu.out
Strawberry Fruit	CA Strawberry	Mb_cast.out
	FL Strawberry	Mb_flst.out
Sweet Potatoes	CA Potato	Mb_capo.out

Crop Grouping	PRZM/EXAMS Crop Scenario	Output File
<u>Tarped Broacast Shank Injection Methyl Bromide Application</u>		
Tomatoes	CA Tomato	Mb_cato.out
Onions	GA Onion	Mb_gaon.out
Golf Courses and Turf	CA Turf	Mb_catf.out
	FL Turf	Mb_fltf.out