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SUBJECT: DEVELOPMENT OF SUB-CHRONIC AIR CONCENTRATION ESTIMATES ASSOCIATED WITH A SINGLE FUMIGANT APPLICATION

Background

The Worker Health and Safety (WHS) branch previously requested air concentration estimates associated with a single fumigant for various sample averaging times less than or equal to 24 hours (hrs) (Barry, 2008). Estimates for iodomethane and chloropicrin were produced for use in the WHS exposure appraisals. The exposure appraisals also include sub-chronic exposure scenarios. Thus, two-week air concentration estimates were requested. For both chloropicrin and iodomethane. In addition, 30-day iodomethane air concentration estimates were requested for comparison with the Air Resources Board (ARB) ambient air concentration data for methyl bromide because the use pattern of iodomethane is expected to be similar to methyl bromide. Thus, the ARB methyl bromide ambient monitoring results can be used as a surrogate for the eventual iodomethane ambient air concentrations.

Methods

The sub-chronic exposure air concentration estimates were produced by extension of the 24 hr air concentration estimates (see Barry, 2008). The same single study flux profiles were used to produce flux profiles of 2-week (chloropicrin and iodomethane) and 30-day duration (iodomethane only). The chloropicrin study flux profiles were based on two-week field studies and were adequate without fitting or extrapolation. Flux profiles for five application methods are available: broadcast/untarp, bed/untarp, bed/tarp, broadcast/tarp, and bed/drip/tarp. (Beard et al., 1996; Rotandardo, 2004). The broadcast/tarp application method has three flux profiles from three separate field studies in Arizona, Washington, and Florida (Table 1).

For iodomethane WHS requested both 2-week and 30-day estimates (Table 2). As part of the registration process the registrant conducted eight studies to characterize the flux profile of iodomethane following application to soil by three different methods: broadcast/tarp, bed/tarp, and drip/tarp (Baker et al., 2001; Baker et al., 2002a; Baker et al., 2002b; Baker et al., 2003; Baker et al., 2004a; Baker et al., 2004b; Baker et al, 2004c). In contrast to the chloropicrin studies, the iodomethane studies were conducted to 10 or 11 days. Consequently, in order to estimate 2-weeks or 30-days, a three parameter lognormal function was fit to the 10 or 11 days iodomethane flux profiles. This function was integrated from the end of measured values out to 14 days or 30 days and the resulting integration added to the measured flux in order to extend the flux estimates out to 2-weeks or 30-days (Table 3).

The procedure to estimate the 2-week and 30-day average air concentration was a follows:

1. Simulate the generic 24-hr centerline downwind air concentrations based on the 100ug/m^2sec generic flux.
2. Adjust the generic 24-hr air concentration to 2-week or 30-day average air concentration. This is the averaging time adjustment factor (development of this adjustment factor will be presented below).
3. Develop each application method flux profile so that it extends for the 2-week or 30-day interval. This is the flux profile development.
4. Calculate the average 24-hr flux over that period and divide by 100. This number represents the average flux on any given day over the 2-week or 30-day interval scaled to the 100ug/m^2sec generic flux.
5. Multiply the 2-week or 30-day average air concentration by the scaled average 24-hr flux to obtain the estimated 2-week or 30-day air concentration for a particular study. This estimates represents the 2-week or 30-day air concentration for an application made at the application rate used in the study.
6. Adjust the 2-week or 30-day air concentration estimate for a particular study to obtain estimates for application rates other than that used in the study.

These steps are illustrated in the EXCEL spreadsheets for iodomethane and chloropicrin in Appendix A.

1. Simulate the generic 24-hour centerline downwind air concentrations

These generic 24-hour centerline downwind air concentration estimates are produced using the 100ug/m^2sec generic flux and the Department of Pesticide Regulation (DPR) standard weather conditions of 1.4 m/s and C stability. See Barry (2008) for method details.

2. Averaging time adjustment factor

The adjustment factors to obtain the 2-week and 30-day average air concentrations from the generic 24-hr air concentrations were derived based upon the U.S. Environmental Protection Agency (EPA) Modeling Guidelines. The 2-week and 30-day average air concentration is the air concentration that would be measured by an air sampler at a particular spot if that air sampler continually drew air over the 2-week or 30-day sampling period.

The basic equation relating air concentrations averaged over different sampling times can be found in Turner (1994) and was reviewed in Barry (2000):

$$\chi_s = \chi_k \left(t_k / t_s \right)^p$$

where:

χ_κ = base concentration
χ_s = desired concentration
t_k = base averaging interval (shorter interval)
t_s = desired averaging interval (longer interval)
p = power law exponent

The adjustment factor, or multiplier is the portion of the equation shown below:

$$\left(t_k / t_s \right)^p$$

The value of p, the power law exponent varies, depending upon the range of averaging times of interest. For example, in U.S. EPA air toxics modeling guidelines (U.S. EPA, 1992a; U.S. EPA, 1992b) the value of p is between 0.096 and 0.29 to obtain the recommended multiplier for adjusting a 1 hr air concentration to between a 3 hr and an annual air concentration. The progression of the values of p and resulting multipliers for adjusting a 1 hour air concentration are shown below:

Averaging Time	Exponent	Multiplier
3 hr	p = 0.096	0.9
8 hr	p = 0.17	0.7
24 hr	p = 0.28	0.4
annual	p = 0.28	0.08

For the sub-chronic exposure assessment an average 24 hr air concentration will be adjusted to a 2 week or a 30 day air concentration. Based upon the above relationships, p = 0.28 is the appropriate exponent value for these adjustments. The multipliers are 0.48 for 2 weeks and 0.39 for 30 days. The justification for this exponent value and the multipliers is shown below.

First, to conform to the U.S. EPA exponent values, adjustment of the 1 hr to 24 hr is as follows:

$$multiplier_{1hr \rightarrow 24hr} = \left(1/24\right)^{0.28} = 0.41$$

The 1 hr to 2 weeks (336 hrs) multiplier:

$$multiplier_{1hr \rightarrow 336hr} = \left(1/336\right)^{0.28} = 0.196$$

The 1 hr to 30 days (720 hrs) multiplier:

$$multiplier_{1hr \rightarrow 720hr} = \left(1/720\right)^{0.28} = 0.158$$

By extension of the equation -

The 24 hr to 2 weeks (336 hrs) multiplier:

$$multiplier_{24hr \rightarrow 336hr} = \left(24/336\right)^{0.28} = 0.48$$

The 24 hr to 30 day (720 hr) multiplier:

$$multiplier_{24hr \rightarrow 720hr} = \left(24/720\right)^{0.28} = 0.39$$

The ratio of the 24 hr multiplier to the 2 week multiplier and the 24 hr multiplier to the 30 day multiplier illustrates that p = 0.28 is the appropriate multiplier for adjusting a 24 hr air concentration to averaging times between 24 hrs and annual:

$$1hr \rightarrow 336hr : 1hr \rightarrow 24hr = 0.196 / 0.41 = 0.48$$

$$1hr \rightarrow 720hr : 1hr \rightarrow 24hr = 0.158 / 0.41 = 0.39$$

3. Flux profile development

Table 3 shows a summary of the subchronic flux estimates for iodomethane. Two of the studies (Guadalupe, drip/tarp and Oxnard, bed/tarp) measured flux that projected 100 percent loss of the applied mass within the 10 days of the application. These measured flux profiles were used "as is" and zeros were used to fill in the remaining days out to 30 days.

For the remaining iodomethane studies a 3 parameter log-normal function was fit to the measured daily flux and used to extend the flux profiles to 30 days. The function was integrated from the end of measured values to 14 days. The resulting flux was added to the measured flux to estimate the 2-week cumulative flux. Similarly, the function was integrated from the end of measured values to 30 days and the result was added to the measured flux to estimate the 30 day cumulative flux.

4. Calculate the average 24-hr flux over the desired period

This number represents the average flux on any given day during the 2-week or 30-day interval. Where necessary the 2-week and 30-day average 24-hr flux estimates were adjusted to prevent projected mass loss from exceeding applied mass. Final flux estimates are shown in Table 3.

5. Multiply the 2-week or 30-day average air concentration by the scaled average 24-hr flux to obtain the estimates 2-week or 30-day air concentration for a particular study

This adjustment scales the generic 2-week or 30-day average air concentration from the 100 ug/m^{2}sec generic flux to the flux observed for the actual study application rate. It is accomplished by dividing the average 2-week or 30-day flux by the 100ug/m^{2}sec generic flux to get a scaled flux value. The generic concentrations are multiplied by the scaled flux value to estimate the 2-week or 30-day air concentration for an application made at the application rate used in the study.

6. Adjust the 2-week or 30-day air concentration estimate for a particular study to obtain estimates for application rates other that that use in the study

Since air concentrations are assumed to be proportional to flux and flux is assumed to be proportional to application rate, 2-week or 30-day air concentration estimates for other application rates can be obtained by applying an adjustment factor that expresses the desired application rate as a proportion of the study application rate.

Results

Appendix A shows results of the procedure for both Chloropicrin and Iodomethane. Appendix B shows the 3 parameter log-normal fits to develop the Iodomethane flux profiles. Appendix C contains the Chloropicrin and Iodomethane flux profiles used to calculate the average 24-hr flux values.

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Table 1. Summary of application rates and flux estimates from chloropicrin studies used to estimate off-site air concentrations.

Study Location	Application Method	Study Application Rate[a] (lb/acre)	Study Effective Broadcast Application Rate (lb/acre)	2-week 24 hr average flux (ug/m^2sec)
Arizona	Broadcast/Untarp	171	171	10.39
Arizona	Bed/Untarp	149	86	5.39
Arizona	Broadcast/Tarp	332	332	12.37
Arizona	Bed/Tarp	377	189	21.45
Washington	Broadcast/Tarp	343	343	9.54
Florida	Broadcast/Tarp	346	346	12.33
California	Bed/Drip/Tarp	300	156	2.24

[a] This application rate is the “treated acre” rate. For broadcast application methods the Study Application Rate and the Study Effective Broadcast Application Rate will be the same. For bed type applications an adjustment must be made to the Study Application Rate to account for the portions of the field that are untreated

Table 2. Iodomethane studies used to estimate off-site air concentrations.

Study	Application Method	Study Treated Acre Application Rate[a]	Study Effective Broadcast Application Rate	175 lb/acre Adjustment Factor	87.5 lb/acre Adjustment Factor
Watsonville, California	Broadcast/Tarp	252	252	0.69	0.35
Manteca, California	Broadcast/Tarp	242	242	0.72	0.36
LaSelva Beach, California	Drip/Tarp	235	162	1.08	0.54
Camarillo, California	Drip/Tarp	175	119	1.47	0.74
Guadalupe, California	Drip/Tarp	174	139	1.26	0.63
Oxnard, California	Bed/Tarp	244	171	1.02	0.51
Guadalupe, California	Bed/Tarp	179	143	1.22	0.61

[a] This application rate is the "treated acre" rate which is only the treated soil area excluding nontreated areas such as furrows. For broadcast application methods the Study Application Rate and the Study Effective Broadcast Application Rate will be the same. For bed type applications an adjustment must be made to the Study Application Rate to account for the portions of the field that are untreated.

Table 3. Summary of the iodomethane 2-week and 30-day factors to estimate the sub-chronic air concentrations.

Study (Application Method)	Study Effective Broadcast Application Rate (lb/ac)	3 Parameter Log-Normal Function R^2 (%)	First Sampling Interval Duration (hrs)	First Sampling Interval Proportion of 24 hrs	Study Reported Measured Proportion Mass Lost	2-week 24 hr average flux (ug/m^{2}sec)	2-week Mass lost (lb/ac)	2-week Proportion of Mass Applied	30-Day 24hr average flux (ug/m^{2}sec)	30-Day Mass Lost (lb/ac)	30-Day Proportion of Mass Applied
Watsonville, California (broadcast/tarp)	252	99.7	22	0.92	0.58	13.58	146.0	0.58	6.48	150.0	0.59
Manteca, California (broadcast/tarp)	242	98.5	19	0.86	0.94	22.1	238.0	0.98	10.47	242.0	1.00
LaSelva Beach, California (drip/tarp)	162	99.9	19	0.86	0.45	7.27	78.4	0.48	3.40	78.5	0.48
Camarillo, California (drip/tarp)	119	99.8	22	0.92	0.83	9.18	98.9	0.83	4.29	99.0	0.83
Guadalupe, California (drip/tarp)	139	-[1]	23	0.96	1.00	12.88	139.0	1.00	6.04	139.0	1.00
Oxnard, California (bed/tarp)	171	-[1]	19	0.86	1.00	15.85	171.0	1.00	7.40	171.0	1.00
Guadalupe, California (bed/tarp)	143	99.9	21	0.87	0.97	12.68	136.8	0.96[2]	5.93	136.9	0.96[2]

[1] These two studies measured flux that results in 100 percent mass loss within the first 10 days.
[2] This mass loss differs slightly from 0.97 due to rounding difference between the study report and calculations in this memorandum.