

Director

Department of Pesticide Regulation



MEMORANDUM

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- FROM:
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 [original signed by E. Kwok]

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DATE: September 8, 2016

SUBJECT: Responses to comments by Dr. Richard A. Fenske on DPR-HHAB's draft 1,3-Dichloropropene Risk Characterization Document dated November 19, 2015

Dr. Richard A. Fenske submitted comments on DPR-HHAB's draft 1,3-Dichloropropene (1,3-D) Risk Characterization Document (RCD) in a memorandum dated November 19, 2015. Dr. Fenske specified that the focus of his review is on the exposure assessment section of the RCD. In general, Dr. Fenske agreed with the approaches used in characterizing the 1,3-D exposures under the occupational and non-occupational settings. The following paragraphs provide his comments which were based on the charge questions posed to reviewers by DPR-HHAB, along with DPR-HHAB's detailed responses.

Hazard Identification and Risk Assessment

<u>Charge question #1</u>: 1. Due to a lack of 1,3-D air monitoring data, DPR estimated certain agricultural handler exposures to 1,3-D using both 1,3-D data and data obtained from chloropicrin exposure studies.

Dr. Fenske comment: As described in "Table IV.4 Data Sources for Exposure Scenarios" (page 104), DPR applied the surrogate data approach for generating exposure estimates of five agricultural handler scenarios: shallow shank application method with tarp, drip application method with and without tarp, application using hand-wand, and tarp remover.

The foundations of the occupational exposure assessments are the measurements drawn from Houtman 1993. The key Houtman data for short-term (STAC) air concentrations appear to be

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five 4-hour TWA measurements collected in Buckeye, AZ in March 1993 for each of the following job tasks: shallow shank application using spill control without tarps, loaders, and reentry activities. 1 found no mention of temperature conditions at the time of this study in the Risk Characterization Document. It may be worth examining this issue, since flux of 1,3-D from soil is sensitive to temperature. Samples were collected in one of the cooler months (March) in the Phoenix area (hot months in the area are May-Oct). However, it may be that the temperatures on the Arizona study days (highs of 29-32 and lows of 6-7 OC) are considered comparable to California Central Valley temperatures when 1,3-D is being applied. It would be helpful to have this issue addressed in the Risk Characterization Document.

DPR-HHAB response: It is likely that temperature affects the magnitude of the flux (Hsieh et al., 1992). However, actually detecting that effect using flux data from field studies is difficult. The sampling period in the flux profile that generates the highest air concentrations, and thus the longest buffer zones, is of most interest for exposure and mitigation analyses. The relationship between the maximum flux and the air temperature measured during the maximum flux sampling interval from the 1,3-D studies used in Johnson (2009) and the Beard (1996) applications used in Beauvais (2010) are shown below. The results are consistent with the assumption that air temperature does not need to be directly considered when using maximum flux measured in field studies. Figure 1 shows all of the applications from Johnson (2009) and Beard (1996). There is no correlation between the air temperature and the magnitude of the flux (r = 0.07, p = 0.81). The Arizona applications from Beard (1996) were subsequently removed from the revised RCD because it was determined that those applications did not meet the new Good Agricultural Practices now on chloropicrin labels (Barry, 2014). Even with removal of the Arizona applications (Figure 2) there is no correlation between air temperature and flux (r = -0.37, p = 0.33).

Figure 1. Relationship between flux (μ g/m²sec) and air temperature during the sampling interval. Applications from Johnson (2009) and Beard (1996).

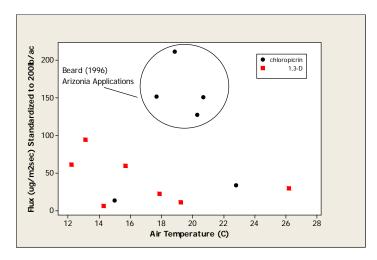
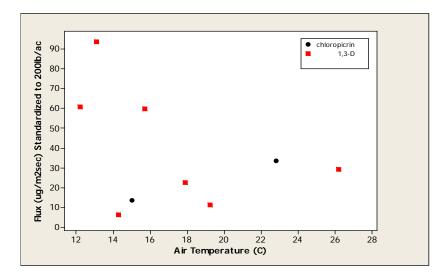


Figure 2. Relationship between flux (μ g/m²sec) and air temperature during the sampling interval. Applications from Johnson (2009) and the Washington and Florida applications from Beard (1996).



In the latest version of the RCD, for estimating short-term exposure, the 95th %-ile was calculated from the natural logarithms of the measured 1,3-D air concentrations from all three (AZ, NC, and WA) study sites. The temperature difference at each location may have had an influence on the exposure estimate. However, temperature differences may occur not only between the study sites and the potential site(s) of interest in CA but also within the state itself. For example, the average low and high temperatures for the month of September in the city of Salinas in Monterey County are 52.9 and 74.7 degrees F, respectively. The corresponding temperatures in the city of Fresno located in Fresno County are 59.7 and 90.8 degrees F (WRCC, 2016). Applications were made in Monterey and Fresno counties during September from 2010-14 (DAS, 2011; DAS, 2012; DAS, 2013; DAS, 2014; DAS, 2015). These temperature differences may cause exposures to differ for workers in the two counties. Differences in wind conditions between the two counties, or even within a county on a given day, also may also have an effect. However, currently there are no modeling techniques available for controlling for these and other meteorological variables for certain exposure scenarios such as the shank applicator or loader. Hence, the exposure estimates must be generated using active ingredient (AI)-specific or surrogate measured air concentration data.

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Dr. Fenske Comment (continued): The seasonal (SAC) and long-term (LAC) air concentrations were based on data from all three of the Houtman study locations (eastern Washington, North Carolina, and Arizona). It is worth noting that all of these studies took place in what were the cooler months in these regions (Oct-Nov in WA; Dec in NC; Mar in AZ). The basic question is whether the temperature conditions in these studies can be considered representative of temperature conditions experienced by workers during 1,3-D applications in California.

<u>DPR-HHAB response</u>: Please see the response to comment above.

Dr. Fenske Comment (continued): The use of the ratio of 95th percentile air concentrations between tasks is an effective means of estimating 1,3-D air concentrations. The very limited sample set available (5 samples for each task at each location) makes it very unlikely that the high range of the sample population distribution was captured.

DPR-HHAB response: We agree with Dr. Fenske that the available 1,3-D air concentration data for use in estimating agricultural handers' exposure may not have captured the highest value. This uncertainty will be communicated to risk managers and the exposures may be further characterized during mitigation.

Dr. Fenske Comment: The chloropicrin air concentrations utilized in the ratio were corrected for recovery and adjusted to the same application rate. One area that might benefit from clarification regards application rate. It is stated that the allowed maximum 1,3-D application rate in California is 332 lbs Al/acre (p.106). However, earlier on this page it is stated that the estimated seasonal application rate is much lower (171 .4 lbs Al/acre). This second number is based on the total number of pounds of 1,3-D applied statewide and the total number of acres treated with 1,3-D statewide in 2012. It is not clear why, for one component of the exposure assessment (STAC) the maximum value is used, whereas for the other components (SAC, AAC and LAC) this statewide average is used. It might be instructive to examine the high use areas in the state (e.g., Merced County, which is the focus on the ambient air concentration exposure assessment) to determine an estimated seasonal application rate to which workers in that county are typically exposed.

DPR-HHAB response: The STAC estimate is for the potential "higher-than-average short-term exposures", which may occur to the worker or residential bystander. The maximum 1,3-D application rate allowed in CA and the upper-bound estimate or 95th percentile of the measured air concentrations, which are assumed to be lognormally distributed, are used to estimate exposure. The short-term exposure estimates cover durations of up to one week (Frank, 2009). However, longer exposures are considered to occur under more typical conditions, as over longer intervals a worker is unlikely to consistently experience high-end exposures. Hence, the SAC, AAC, and LAC are estimated using the estimated seasonal application rate and the mean of the measured air concentrations. In the latest version of the RCD, the use of the AGRIAN® pesticide use report database allowed for estimation of seasonal application rates specific to the application method in the highest use county for that method.

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<u>Charge question #2</u>: DPR employed a scaling approach for estimating residential bystanders exposures to 1,3-D due to shallow shank, deep shank, and drip application methods.

Dr. Fenske Comment: As discussed in "Residential Bystander Exposure Estimates (Edge of Buffer Zone)" (page 118), the 1,3-D air concentrations at 100 feet downwind from shallow shank, deep shank, or drip applications were generated using Industrial Source Complex Short-Term Model version 3 (ISCST3) with a nominal flux of 100 μ g/m²/s for all applications and all field sizes. This modeling approach allows for scaling of the air concentration from a given application rate of 1,3-D employed in the modeling to the maximum rate allowed.

The selection of 100 feet downwind to estimate 1,3-D air concentrations from various application techniques is an appropriate distance, since product labels and California permit conditions mandate a 100-foot buffer zone between fumigated fields and occupied structures. Use of ISCST3 to generate exposure estimates is sound scientific practice. The Industrial Source Complex Short-Term Model has been tested and is used by the US Environmental Protection Agency to generate air concentration estimates for a variety of scenarios. Scaling based on maximum allowable application rates (pounds per acre) is a sound scientific method for the generation of estimated air concentrations for different application methods (shallow shank, deep shank and drip).

DPR-HHAB response: No response necessary.

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<u>Charge question #3</u>: DPR evaluated the lifetime exposure to 1,3-D by individuals residing in a high 1,3-D use area using simulated 1,3-D air concentrations coupled with stochastic human exposure assessment models: Monte Carlo Annual-Based Lifetime Exposure model (MCABLE) and High-End Exposure version 5, Crystal Ball (HEE5CB).

Dr. Fenske Comment: The simulated air concentrations of 1,3-D were generated by Soil Fumigant Exposure Assessment System (SOFEA@) version 2 (SOFEA-2) (page 122).

SOFEA is an air dispersion model for soil fumigants developed by the registrant. Most of the documents that describe this model were not accessible to reviewers (Cryer and van Wesenbeeck 2000a; 2000b; Cryer et al. 2004; 2015; van Wesenbeeck and Cryer 2014; van Wesenbeeck et al. 2015). However, a thorough description of SOFEA available in the peer-reviewed literature was reviewed (van Wesenbeeck et al. 2011. J Environ Qual 40:1462-69), and Appendix 5 of the Risk Characterization Document provided a helpful overview and analysis of SOFEA-2. The retrospective comparison of SOFEA outputs to the CARB/CDPR monitoring study in Parlier (van Wesenbeeck et al. 2011) demonstrated that the model performed well against observed measurements. This suggests that SOFEA may be a useful model to more generally to estimate 1,3-D air concentrations that result from soil fumigation. Appendix 5 (August 12, 2015 CDPR Review of SOFEA 2) identifies several deficiencies in SOFEA-2. In particular the review found that atmospheric stability classes assigned for many hours were in error, and that mixing height adjustments for many hours were in error. Since this review is dated just 19 days earlier than the Risk Characterization Document, it is not clear if the simulated air concentrations generated for this risk assessment took into account these concerns.

DPR-HHAB response: It is true that the simulated air concentrations of 1,3-D used in the RCD did not incorporate corrections to the errors identified in SOFEA-2 (Appendix 5). However, on page 163 in the draft RCD, we noted concerns about these errors and considered that they may have contributed to the observations that for Township #2 and #5, <0.1% of the simulated values are greater than the observed. Currently, we are working on correcting these errors in the SOFEA-2; the revised SOFEA-2 will be used to update the needed air concentrations for use in developing mitigation measures.

Dr. Fenske comment (continued): One important factor noted in van Wesenbeeck et al. (2011) was 1,3-D volatilization due to warmer temperatures. The article states: "Cumulative mass loss between cool (22 September-21 June) and warm (22 June-21 September) season was increased from 26 to 40% (a scaling factor of 1.6) for the soil fumigant 1,3-D (Cryer and van Wesenbeeck, 2001) to account for increased volatilization due to warmer soil temperatures, although this scaling factor has not been validated by lab or field measurements." It is not clear whether this scaling factor has been validated or modified since 2011, or whether the current version of SOFEA (SOFEA-2) uses this or a different scaling factor.

DPR-HHAB response: The seasonal scaling factor of 1.6 is used in the current SOFEA-2 model. According to Johnson (2013), this scaling factor was based upon analysis of 1,3-D flux measured in Knuteson et al. (1992) and Knuteson et al. (1995). The 1.6 seasonal adjustment factor was an ad hoc adjustment for assumed higher flux in summer because Knuteson et al. (1992) and Knuteson et al. (1995) were conducted in fall and spring, respectively (Bruce Johnson, personal communication January 24, 2016).

Dr. Fenske comment: The exposure estimates were generated using two stochastic human exposure assessment models: MCABLE and HEE5CB (page 123); the main differences between these models are the volume of data used per simulation (11664 values in HEE5CB versus 1.16 million values in MCABLE) (page 131) and residential-mobility assumptions employed for estimating exposures (page 129-131). HEE5CB has a more restrictive assumption than MCABLE in the time that an individual lives (i.e., residency) and spends (i.e., mobility) within different townships in a high 1,3-D use area.

The Kaplan survey appears to have had very low response rates (quotient of those participated in interviews and the sum of those who participated and those who refused to participate in interviews). The response rate for Merced County, for example, was 6.9%. There is no evidence presented in the Kaplan report to indicate that this very small fraction of those who were contacted is representative of the county population. Thus, it is difficult to ascertain the reliability of these survey results.

DPR-HHAB response: We agree that it is difficult to ascertain the reliability of these survey results. Therefore, we employed a human exposure assessment method (i.e., HEE5CB) that is independent of the survey results of Kaplan for characterizing lifetime 1,3-D exposure to humans.

Dr. Fenske Comment: In some cases, SOFEA-2 may have under-predicted the concentrations of 1,3-D (Table V. 6 [page 164)). To minimize the potential impact of the air concentration under-predictions, only the simulation air concentrations with annual average values equal to or higher than the observed mean value were included in the human exposure modeling (page 163).

The decision to use a subset of the 100 air concentration simulation results produced by SOFEA-2 as inputs for the HEE5CB model seems appropriate, given the very low frequency of simulated results exceeding observed values in Townships 2 and 5. As stated, the infrequent occurrence of high 1,3-D concentrations could result in under-predictions. However, the criterion adopted - only simulation air concentrations with annual average values equal to or higher than the observed mean value - resulted in exclusion of more than two-thirds (69) of the 100 values, and may lead to some over-prediction. One can imagine other criteria; e.g., all values within 25% of the observed mean value or higher. It would be useful to provide some additional discussion of the rationale that underlies selection of the criterion used.

DPR-HHAB response: We concur with Dr. Fenske's concern. To address his points, we included all 100 lists of average annual air concentrations for performing the human exposure assessment simulation using MCABLE model. As stated in the draft RCD (Page 163), to minimize the potential impact of infrequent occurrence of high 1,3-D air concentrations in SOFEA-2 predictions, we selected the lists of 31 average annual air concentrations whose ranges that bracketed the mean observed value in Township #5 for use in another human exposure assessment simulation model: HEE5CB. This criterion is set based on the observation that residents in Township #5 experienced the highest measured 1,3-D concentrations in Merced, CA. We agree that the decision to exclude some data in the HEE5CB simulation may result in some over-prediction. However, since the inclusion of all data in MCABLE may result in some under-prediction, the "over-prediction of HEE5CB" and "under-prediction of MCABLE" may provide a range of realistic estimates of human exposures to 1,3-D. We have modified the text to elaborate this concept as suggested.

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References

- Barry, T. 2014. Development of chloropicrin buffer zones revised. Memorandum dated October 31, 2014 to <u>David Duncan, Environmental Program Manager II. Environmental</u> <u>Monitoring Branch. Department of Pesticide Regulation. California Environmental</u> <u>Protection Agency. 1001 I Street. P.O. Box 4015. Sacramento, California 95812-4015.</u> <<u>http://www.cdpr.ca.gov/docs/whs/pdf/appendix_4_buffer_zones_memo.pdf.></u>
- Beard, K. K., Murphy, P.G., Fontaine, D.D. and Weinberg, J.T. 1996. Monitoring of Potential Worker Exposure, Field Flux, and Off-Site Air Concentration During Chloropicrin Field Application. Lab Project Number: HEH 160. Unpublished study submitted by Chloropicrin Manufacturers Task Force. MRID 441492-01.
- Beauvais, S. 2010. Chloropicrin Soil fumigation Occupational Exposure Data. Memorandum dated July 29, 2010 to Joseph P. Frank, Senior Toxicologist. Worker Health and Safety Branch. Department of Pesticide Regulation. California Environmental Protection Agency. 1001 I Street. P.O. Box 4015. Sacramento, California 95812-4015. http://www.cdpr.ca.gov/docs/whs/memo/hsm10005.pdf
- DAS 2011. Historical Use Data of Adjusted Pounds of 1,3-Dichloropropene in Calfornia from 1995 to 2010 (CD). IN (5796) Dow AgroSciences (DPR Vol. No. 50046-0196).
- DAS 2012. Historical Use Data of Adjusted Pounds of 1,3-Dichloropropene in Calfornia from 1995 to 2011 (CD). IN (5796) Dow AgroSciences (DPR Vol. No. 50046-0199).
- DAS 2013. Historical Use Data of Adjusted Pounds of 1,3-Dichloropropene (1,3-D) in Calfornia, 1995-2012 (Township Cap Data) (CD) IN (5796) Dow AgroSciences (DPR Vol. No. 50046-0205).
- DAS 2014. Historical Use Data of Adjusted Pounds of 1,3-Dichloropropene (1,3-D) in California, 1995-2012 (Township Cap Data) (CD) IN (5796) Dow AgroSciences (DPR Vol. No. 50046-0211). . In *Dow Agrosciences LLC* Dow Agrosciences Indianapolis, IN (5796).
- DAS 2015. 1,3-Dichloropropene Historical Use Data in California from 1995-2014 (CD). Dow Agrosciences LLC,Indianapolis, IN (5796) 50046-0224.
- Frank, J. P. 2009. Method for Calculating Short-Term Exposure Estimates. Worker Health and Safety Branch, Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. <<u>http://www.cdpr.ca.gov/docs/whs/memo/hsm09004.pdf</u>.>

- Gillis, M. J., and Dowling, K. C. 1998. Effect of broadcast and row application methods on 1,3dichloropropene emissions. Indianapolis, Indiana 46268: Dow AgroSciences HEA95177. DPR Vol. No. 50046-127.
- Hsieh, D.P.H, J.N. Seiber, and J.E. Woodrow. 1992. Pesticides in Air. Part II: Development of predictive methods for estimating pesticide flux to air. Final Report. Contract No. 92-313. California Air Resources Board. Research Division. P.O. Box 2815. Sacramento, CA 95812. < <u>http://www.arb.ca.gov/research/apr/past/92-313pt2.pdf</u>>
- Johnson, B. 2009. Calculation of screening concentrations for 1,3-Dichloropropene. Memorandum dated December 2, 2009 to Joseph P. Frank, Senior Toxicologist. Worker Health and Safety Branch. Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA 95812-4015. <<u>http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/4467_johnson.pdf</u>>
- Johnson, B. 2013. Calculation of use adjustment factors for 1,3-Dichloropropene with the use of totally impermeable film for broadcast shank applications. Memorandum dated April 26, 2013 to Randy Segawa, Environmental Program Manager I. Environmental Monitoring Branch. Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA 95812-4015.
 http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/2444_dichlor_film_application.pdf>
- Knuteson, J. A., Dixon-White, H. E., and Petty, D. G. 1995. Field volatility of 1,3dichlororopropene in San Joaquin Valley California. Dow Agrosciences Indianapolis, In (5796) Dow Agrosciences (DPR Vol. No. 50046-0088 Record No. 134784).
- Knuteson, J. A., and Dolder, S. C. 2000. Field volatility of 1,3-dichloropropene and chloropicrin from shallow drip irrigation application of Telone C-35 (InLine) to strawberry beds covered with VIF tarp. In *Dow Agrosciences* Dow Agrosciences Indianapolis, IN (5796)
- Knuteson, J. A., Petty, D. G., and Shurdut, B. A. 1992a. Field volatility of 1,3-dichloropropene in Salinas Valley California. Midland, MI 48674: DowElanco ENV91011. (DPR Vol. No. 50046-0067, Record No. 120011). 50046-0067.
- Knuteson, J. A., Petty, D. G., and Shurdut, B. A. 1992b. Field Volatility of 1,3-dichloropropene in the Imperial Valley of southern California. Midland, MI 48641-1706: DowElanco ENV91001. (DPR Vol. No. 50046-0053, Record No. 113745). 50046-0053.

- Sanborn, J. R., and Powell, S. 1994. Human Exposure Assessment for 1,3-dichloropropene, pp. 29. California Environmental Protection Agency, Department of Pesticide Regulation, Worker Health and Safety Branch, 1020 N Street, Sacramento California 95814.
- van Wesenbeeck, I., and Phillips, A. M. 2000. Field volatility of 1,3-dichloropropene and chloropicrin from surface drip irrigation application of In-Line to vegetables beds under polyethylene tarp. Indianapolis, Indiana 46268-1054: Dow AgroSciences LLC 990072. (DPR Vol. No. 50046-152, Record No. 178246). 50046-152.