Appendix 4

Studies Excluded From the Department of Pesticide Regulation's Evaluation of Fumigant Volatile Organic Compound Emissions

Fumigant	Reference	Comment
Methyl Bromide	Gan, J., S.R. Yates, D. Wang, and W.F. Spenser. 1996. Effect of soil factors on methyl bromide volatilization after soil application. Environ. Sci. Technol. Vol 30:1629-1636.	Soil column study. It has not been reliably demonstrated that soil column results reflect field scale results
	Gan, J., S.R. Yates, W.F. Spenser, M.V. Yates, and W.A. Jury. 1997. Laboratory-scale measurements and simulations of effect of application methods on soil methyl bromide emissions. J. Environ. Qual. Vol 26:310-317.	Soil column study. It has not been reliably demonstrated that soil column results reflect field scale results.
	Majewski, M.S., M.M. McChesney, J.E. Woodrow, H.H. Prueger, and J.N. Seiber. 1995. Aerodynamic measurements of methyl bromide volatilization from tarped and nontarped fields. J. Environ. Qual. Vol 24:742-752.	Results from these applications are already included in the DPR MeBr database as DPR studies.
	Yagi, K., J. Williams, N.-Y. Wang, R.J. Cicerone. 1995. Atmospheric methyl bromide (CH_3Br) from agricultural soil fumigations. Science Vol 267:19791981.	This study used chambers to measure flux. Flux results from this experiment differ significantly from a previous study by the same authors using the same application method (34% mass loss vs. 89% mass loss). Source of the difference was not adequately established and may simply be due to the large variation observed when measuring flux by the chamber method.
	Yates, S.R., J. Gan, F.F. Ernst, A. Mutzinger, and M.V. Yates. 1996. Methyl bromide emissions from a covered field: I. Experimental conditions and degradation in soil. J. Environ. Qual. Vol 25:184-192.	Although air concentrations were measured on a central mast, no flux estimates were included in the paper. The second paper (below) presents the flux estimates. In this paper, total mass loss was estimated only by soil bromine measurements. DPR has not used soil bromine measurements to estimate flux and mass loss.
	Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and M.V. Yates. 1996. Methyl bromide emissions from a covered field: I.I Volatilization. J. Environ. Qual. Vol 25:192-202.	The air mast sampling timeline is not clearly shown in either of the papers in this set. The text of part I states that the application duration was 6.5 hrs and that the application was interrupted to install the sampling equipment on the field. This seems to indicate that ½ of the application was not sampled. The authors state in the conclusions that large levels of emissions result when MeBr is applied at shallow depth and the soil covered with relatively permeable polyethylene tarp. Thus, due to the delay in beginning sampling, the flux estimates may be biased low. Even if these results were included, the loss estimate would not be different from that obtained using the DPR data base exclusively.

	Yates, S.R., D. Wang, F.F. Ernst, and J. Gan. 1997. Methyl bromide emissions from agricultural fields: Bare-soil, deep injection. Environ. Sci. Tech. Vol 31:1136-1143.	No air samples for direct flux methods were taken during the 4 hour application. The authors note that the soil bromine measurements estimate a 21% mass loss while the direct flux methods estimate mass loss between 2% and 5%. The authors speculate that the difference in mass loss was due to emissions during the application. The authors list 21% as the mass loss in a subsequent journal article (phytopathology vol 92(12):1344-1348) indicating that they have placed more weight on the soil bromine estimate. In addition, the 68cm injection depth is 8cm deeper than usual practice of 60cm.
	Yates, S.R., J. Gan, F.F. Ernst, D. Wang, and M.V. Yates. 1996. Emissions of methyl bromide from agricultural fields: Rate estimates and methods of reduction. In: J.N. Seiber, J.A. Knuteson, J.E. Woodrow, N.L. Wolfe, M.V. Yates, and S.R. Yates (Eds). Fumigants: Environmental fate, exposure, and analysis. ACS Symposium Series 652. American Chemical Society, Washington, DC. pp 116-134.	This book chapter summarizes result presented in other papers. No new data is presented.

1,3-D	Gao, S. and T.J. Trout. 2006. Using surface water application to reduce 1,3-dichlorpropene emissions from soil fumigation. J. Environ. Qual. Vol 35:1040-1048.	This paper reports results from soil column experiments using only 1,3-D. The treatments: A. Dry soil/no tarp/no water B. Initial water before fumigant injection/no tarp C. Treatment B + more water applied to soil surface at 12 hrs post injection D. Treatment C + more water applied to soil surface at 24 hrs post injection E. Dry soil covered with HDPE F. Treatment B covered with HDPE G. Dry soil covered with VIF Factors that limit the use of these results in the VOC program: 1) The dry soil applications do not follow Telone label instructions and thus, do not reflect practices required by applicators in the field. 2) Treatments C and D required that the soil column be opened in order for the additional water to be applied to the soil surface. The authors adjust for the speculated effect of the disturbance of the equilibrium in the soil column. However, there was no control column that was opened with no water applied. Therefore, it is impossible to assign the response observed in the emissions to the water rather than the disturbance of the soil column headspace and equilibrium (or some interaction between the two). The authors argue that after the first sample following the opening of the soil column following samples "…should not have been affected…" however, nothing is presented to support that assertion. The lack of a control for this procedure likely invalidates the results of those treatments.

	Gao, S. and T.J. Trout. 2007. Surface seals reduce 1.3-dichloropropene and chloropicrin emissions in field tests. J. Environ. Qual. Vol 36:110-119.	Treatments i) control – dry soil ii) dry soil covered with HDPE iii) dry soil covered with VIF iv) Initial water before fumigant injection/covered with HDPE v) Dry soil injection followed by water application/no tarp vi) Treatment v + additional intermittent water at 8, 22, 28, 32, and 48hr Factors that limit the use of these results in the VOC program: 1) The dry soil applications (i, ii, and iii) do not follow Telone label instructions and thus, do not reflect practices required by applicators in the field. 2) The intermittent water treatment (vi) pattern is not a reasonable procedure for applicators to follow. There is no way to reliably adjust the experimental results to reflect a more reasonable intermittent watering pattern. 3) Plots were different sizes. The water treatment plots were 9m x 9m. The tarp treatments were 9m x 3m. 4) The plots are separated by 3m buffers. This is very close. It is possible that the water applications to the neighboring plots changed the flux dynamics on the dry plots due to local changes in humidity. 5) Emission measurements were taken using chambers. The authors speculate about the reliability of chamber results, particularly for the dry soil treatments (giving one more reason to not use the dry soil results). They state: "We highly suspect that the passive chamber method might underestimate fumigant emissions from a bare and dry soil surface because a perfect seal between the chamber and the soil was difficult to form during the 30 min capture time." This section of the text that casts doubt on the reliability of the results. 6) The 30 min capture time is also an issue. These are snap-shots in time and how well they characterize loss over longer periods is not discussed. 7) No emission measurements were taken at night. The authors speculate that the control treatment peak flux occurred at night because for both 1,3-D and chloropicrin the total control mass loss is less than HDPE loss. They also speculate that the peak flux for the HDPE treatment occurred early in the morning when no measurements were taken. However, they do not apply the same speculation to any of the other treatments. Due to the study design, the flux profiles are not adequately characterized.

	van Wesenbeeck, I.J., C.K. Robb and D.A. Lindsay. 1998. Field volatility of 1,3-dichloropropene from an untarped buried drip application in the Rio Grande Valley of Texas Amended Report. Study ID ENV97106 Dow AgroSciences LLC, Indiana.	This study was not used for the following reasons: 1) puddling on downwind portion of field led to inconsistency between concentrations and fluxes and created uncertainty in the flux (2) study was untarped (current label requires tarping)
Chloropicrin	Gan, J., S.R. Yates, F.F. Ernst, and W.A. Jury. 2000. Degradation and volatilization of fumigant chloropicrin after soil treatment. J. Environ. Qual. Vol 29:1391-1397.	Soil column study. Has not been reliably demonstrated that soil column results reflect field scale results
	Gao, S. and T.J. Trout. 2007. Surface seals reduce 1.3-dichloropropene and chloropicrin emissions in field tests. J. Environ. Qual. Vol 36:110-119.	See comments for this article in the 1,3-D section above.
	Gillis, M. and G.S. Smith. 2002. Chloropicrin emissions and offsite drift from tarped and non-tarped fields treated by a drip irrigation application method. Study TC350. Unpublished report submitted to CDPR. DPR Registration Volume 199-0114.	This study was not used because the quality assurance/quality control data submitted in support of the study results was not of acceptable quality.
	Lee, H., K.V. Natta, and M. Gillis. 1994.. Chloropicrin worker exposure, flux, and offsite monitoring and dispersions modeling for tarped broadcast application – pilot study. Study TC246/BR707. Unpublished report submitted to CDPR. DPR Registration Volume 199-0079.	This study was not used for the following reasons: 1) No acceptable quality assurance/quality control data was include in the report, 2) no table showing the flux calculations was included in the report, 3) dispersion modeling underestimated the observed concentrations indicating that the flux estimates were low.
	Wang, D., J. Juzwik, and S. Fraedrich, K. Spokas, Y. Zhang, and W.C. Koskinen. 2005. Atmospheric emissions of methyl Isothiocyanate and chloropicrin following soil fumigation and surface containment treatment in bare-root forest nurseries. Can. J. For. Res. Vol 35:1202-1221.	This study was not included because flux was estimated using passive chambers. Due to significant technical issues with chamber sampling DPR has elected to omit flux estimates obtained using chambers.
	Zhang, Y. and D. Wang. 2007. Emission, distribution, and leaching of methyl Isothiocyanate and chloropicrin under different surface containments. Chemosphere 68:445-454.	Soil column study. It has not been reliably demonstrated that soil column results reflect field scale results.

Metam Sodium	Zhang, Y. and D. Wang. 2007. Emission, distribution, and leaching of methyl Isothiocyanate and chloropicrin under different surface containments. Chemosphere 68:445-454.	Soil column study. It has not been reliably demonstrated that soil column results reflect field scale results.
	Sullivan, D.A., M.T. Holdsworth, H. Ajwa, S. Nelson, D. Dickson. 2003. Draft Report. Citra, Florida studies of incorporation and drip irrigation with tarping. Submitted September 24, 2004 on behalf of the Metam Sodium Task Force. DPR Registration Volume number 50150-0159.	This study was not included for the following reasons: 1) the application and mitigation methods are not adequately described, 2) there is no quality assurance/quality control data included, 3) only a summary of estimation of flux is provided so no review is possible, 4) even if the information to fully review the flux estimates was submitted, the summary indicates that the flux back-calculation used log-transformed data which is not acceptable.
	Sullivan, D.A. and M.T. Holdsworth. 2004 Study of Roozen shank injection rig at Washington Bulb Co. site, Mount Vernon, Washington. Submitted September 24, 2004 on behalf of the Metam Sodium Task Force. DPR Registration Volume number 50150-0158.	This study was not included for the following reasons: 1) the application and mitigation methods are not adequately described, 2) there is no quality assurance/quality control data included, 3) only a summary of estimation of flux is provided so no review is possible, 4) even if the information to fully review the flux estimates was submitted, the summary indicates that the flux back-calculation used log-transformed data which is not acceptable.
	Sullivan, D.A. and M.T. Holdsworth. 2001. Orange County drip application study modeling results prepared for the Metam-Sodium Task Force. Sullivan Consulting, Inc. 1900 Elkin Street, Suite 249, Alexandria, VA 22308. Report dated December 18, 2001.	This study was not included because it is a pilot study that employed minimal air concentration sampling not sufficient to reliably estimate flux. In addition, at the time of application the soil was not within the labeled moisture range. There is no quality assurance/quality control data submitted.
	Sullivan, D.A. and M.T. Holdsworth. 2001. Lancaster pilot study of intermittent sealing for a sprinkler irrigation application . Prepared for the Metam Sodium Task Force Sullivan Consulting, Inc. 1900 Elkin Street, Suite 249, Alexandria, VA 22308. Report dated December 18, 2001.	This study was not included because it is a pilot study that employed minimal air concentration sampling not sufficient to reliably estimate flux. The application plots were very narrow rectangles that could significantly affect the results. There is no quality assurance/quality control data submitted.
	Sullivan, D.A. and M.T. Holdsworth. 2001. Santa Barbara County pilot study of intermittent sealing for a shank injection application. Prepared for the Metam Sodium Task Force Sullivan Consulting, Inc. 1900 Elkin Street, Suite 249, Alexandria, VA 22308. Report dated December 18, 2001.	This study was not included because it is a pilot study that employed minimal air concentration sampling not sufficient to reliably estimate flux. The application plots were very narrow rectangles that could significantly affect the results. There is no quality assurance/quality control data submitted.
	Sullivan, D.A. and M.T. Holdsworth. 2001. Panama Lane pilot study of intermittent sealing for a chemigation application . Prepared for the Metam Sodium Task Force. Sullivan Consulting, Inc. 1900 Elkin Street, Suite 249, Alexandria, VA 22308. Report dated December 18, 2001.	This study was not included because it is a pilot study that employed minimal air concentration sampling not sufficient to reliably estimate flux. The application plots were very narrow rectangles that could significantly affect the results.
	Edison Road 2005. Early start/sunset seal	This study has not been submitted to DPR
	USDA Salinas 2004 Shank/tarp	This study has not been submitted to DPR
	USDA Salinas 2004 Drip/tarp	This study has not been submitted to DPR

	Brawley 2004 Flood	This study has not been submitted to DPR
	USDA 2002 Bakersfield shank	This study has not been submitted to DPR
	USDA 2002 Bakersfield chemigation	This study has not been submitted to DPR
	Firebaugh 1992 chemigation	This study has not been submitted to DPR.
	ARB. 1993. Ambient air monitoring in Contra Costa County during March 1993 after an application of Metam Sodium to a Field. Test Report No. C92-070A. July 14, 1993. http://www.cdpr.ca.gov/docs/emon/pubs/tac/tacpdfs/metamsod.pdf	This study was not designed to estimate flux. Air sampling is insufficient and the meteorological data is not available.
	ARB. 1993. Ambient air monitoring for MITC in Kern County during summer 1993. Test Report No. C92-070. April 27, 1994. http://www.cdpr.ca.gov/docs/emon/pubs/tac/tacpdfs/mitckern.pdf	This study was not designed to estimate flux. Air sampling is insufficient and the meteorological data is not available.
	Wang, D., J. Juzwik, and S. Fraedrich, K. Spokas, Y. Zhang, and W.C. Koskinen. 2005. Atmospheric emissions of methyl Isothiocyanate and chloropicrin following soil fumigation and surface containment treatment in bare-root forest nurseries. Can. J. For. Res. Vol 35:1202-1221.	This study was not included because flux was estimated using passive chambers. Due to significant technical issues with chamber sampling DPR has elected to omit flux estimates obtained using chambers.
	Zhang, Y. and D. Wang. 2007. Emission, distribution, and leaching of methyl Isothiocyanate and chloropicrin under different surface containments. Chemosphere 68:445-454.	Soil column study. It has not been reliably demonstrated that soil column results reflect field scale results.