





State Water Resources Control Board

March 04, 2014

David Duncan, Chief Environmental Monitoring Branch Pesticide Programs Division Department of Pesticide Regulation 1001 "I" Street, Floor 3 Sacramento, California 95814

Dear Mr. Duncan:

EXTERNAL PEER REVIEW OF THE DEPARTMENT OF PESTICIDE REGULATION'S METHODOLOGY TO DEVELOP BUFFER ZONES AND MITIGATION MEASURES FOR CHLOROPICRIN

This letter responds to the attached November 14, 2013 request for external scientific peer review for the subject noted above. The review process is described below. All steps were conducted in confidence. Reviewers' identities were not disclosed.

To begin the process for selecting reviewers, I contacted the University of California, Berkeley (University) and requested recommendations for candidates considered qualified to perform the assignment. The University was provided with the November 14, 2013 request letter to me and attachments. The request was later augmented with the January 27, 2014 request letter to me and attachments. The University concurred that the augmented request was appropriate, and no additional material was asked for. This service by the University includes interviews of each promising candidate and is supported through an Interagency Agreement cosigned by Cal/EPA and the University.

Each candidate who was both interested and available for the review period was asked to complete a Conflict of Interest (COI) Disclosure form and send it to me for review, with Curriculum Vitae. The cover letter for the COI form describes the context for COI concerns that must be taken into consideration when completing the form. "As noted, staff will use this information to evaluate whether a reasonable member of the public would have a serious concern about [the candidate's] ability to provide a neutral and objective review of the work product."

In subsequent letters to candidates approved as reviewers, I provided the attached January 7, 2009 Supplement to the Cal/EPA Peer Review Guidelines, which, in part serves two purposes: a) it provides guidance to ensure confidentiality through the course of the external review, and, b) it notes reviewers are under no obligation to discuss their comments with third-parties after reviews have been submitted. We recommend they do not. All outside

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parties are provided opportunities to address a proposed regulatory action, or potential basis for such, through a well-defined rulemaking process.

Later, I sent each reviewer the material to be reviewed and a detailed cover letter to initiate the review (examples attached).

Also, attached to the cover letter was the November 14, 2013 request for reviewers to me. Its Attachment 2 was highlighted as the focus for the review. Each reviewer was asked to address each topic, as expertise allows, in the order given. Fifty days were provided for the review. I also asked reviewers to direct enquiring third-parties to me after they have submitted their reviews.

I subsequently sent the January 27, 2014 augmentation request to each reviewer. This added a fifth conclusion to be reviewed. The request included an attachment of eight references which could be accessed electronically.

Reviewers' names, affiliations, curriculum vitae, and reviews are being sent to you now with this letter. All attachments can be electronically accessed through the bookmark icon at the left of the screen.

Approved reviewers are as follows:

Mingxin Guo, Ph.D.
 Professor of Soil and Water Sciences
 Department of Agriculture and Natural Resources
 Delaware State University
 15 Baker Building
 Dover, DE 19901

Telephone: 302-857-6479 FAX: 310-857-6455 Email: mguo@desu.edu

2. Glenn C. Miller, Ph.D.

Professor, Department of Natural Resources and Environmental Science Director, Graduate Program in Environmental Science University of Nevada, Reno 1664 North Virginia Street Reno, NV 89557

Telephone: 775-784-4108 FAX: 775-784-4583 Email: glennm@unr.edu

3. James N. Seiber, Ph.D.

Editor-in-Chief, Journal of Agricultural and Food Chemistry Department of Environmental Toxicology, Emeritus Professor University of California, Davis One Shields Avenue Davis, CA 95616 Telephone: 530-752-1141 FAX: 530-752-4759

Gerald W. Bowes

Email: jnseiber@ucdavis.edu

If you have questions, or require clarification from the reviewers, please contact me directly.

Regards,

Gerald W. Bowes, Ph.D.

Manager, Cal/EPA Scientific Peer Review Program Office of Research, Planning and Performance State Water Resources Control Board 1001 "I" Street, 16th Floor

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Attachments

- 1) November 14, 2013 Request by David Duncan for Scientific Peer Review
- 2) Example of Letter to Reviewer Initiating the Review
 - a) Mingxin Guo, Ph.D., Delaware State University
 - b) Glenn C. Miller, Ph.D., University of Nevada, Reno
 - c) James N. Seiber, Ph.D., University of California, Davis
- 3) January 7, 2009 Supplement to Cal/EPA Peer Review Guidelines
- 4) January 27, 2014 Request by David Duncan to Amend the November 14, 2013 Scientific Peer Review Request
- 5) Curriculum Vitae:
 - a) Mingxin Guo, Ph.D., Delaware State University
 - b) Glenn C. Miller, Ph.D., University of Nevada, Reno
 - c) James N. Seiber, Ph.D., University of California, Davis
- 5) Reviews:
 - a) Mingxin Guo, Ph.D., Delaware State University
 - b) Glenn C. Miller, Ph.D., University of Nevada, Reno
 - c) James N. Seiber, Ph.D., University of California, Davis

ec: Randy Segawa, Environmental Program Manager Department of Pesticide Regulation Randy.Segawa@cdpr.ca.gov

Department of Pesticide Regulation



Brian R. Leahy Director

MEMORANDUM

TO: Gerald W. Bowes, Ph.D.

> Manager, Cal/EPA Scientific Review Program Office of Research, Planning and Performance

State Water Resources Control Board

1001 I Street, MS 16B

Sacramento, California 95814

FROM: David Duncan, Environmental Program Manager

Environmental Monitoring Branch

916-445-3870

DATE: November 14, 2013

SUBJECT: REQUEST FOR AN EXTERNAL PEER REVIEW OF THE DEPARTMENT OF

PESTICIDE REGULATION'S METHODOLOGY TO DEVELOP BUFFER ZONES

Original Signed By

AND MITIGATION MEASURES FOR CHLOROPICRIN

In accordance with Health and Safety Code section 56004, the California Department of Pesticide Regulation (DPR) requests external peer review of its methodology entitled "Development of Chloropicrin Buffer Zones." The methodology consists of analysis of field monitoring data performed to provide a basis for California buffer zone development. DPR will use the document to support future mitigation measures for chloropicrin, but regulations are not in development at this time.

For this peer review, I suggest that the reviewers have expertise in the following areas, in order of importance:

- 1. Statistics distributional analysis
- 2. Air quality / air pollution modeling
- 3. Environmental chemistry

We estimate that three reviewers will be adequate to cover all needed areas of expertise.

The documents are ready for review at any time, and the preferred period of review is 60 days.

The following attachments are enclosed:

- Attachment 1: Plain English summary of the proposal, "Development of Chloropicrin Buffer Zones."
- Attachment 2: Description of scientific assumptions, findings, and conclusions to review.
- Attachment 3: List of Participants.
 - o A. California Department of Pesticide Regulation Staff
 - o B. Other Participants
 - o C. Participants who Provided Comments During Public Comment Period
 - o D. Bibliography

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If you have any questions regarding this request, please contact Randy Segawa, at 916-324-4137 or at <rsegawa@cdpr.ca.gov>. Thank you for your time and consideration of this request.

Attachments

cc: Randy Segawa, DPR Environmental Program Manager (w/Attachments)

Attachment 1 Plain English Summary of "Development of Chloropicrin Buffer Zones"

DPR identified chloropicrin as a Toxic Air Contaminant (TAC) and determined that mitigation measures are needed to reduce exposures. DPR completed a Risk Characterization Document (RCD) for chloropicrin as a TAC in February 2010. Focusing on residents and bystander exposure, the RCD assessed the health risk of chloropicrin based on evaluations of toxicology studies, and exposure estimates from air monitoring, computer modeling, and other data. In December 2010, DPR issued a Risk Management Directive that identified some unacceptable exposures in the RCD, and directed staff to develop use restrictions. DPR's Risk Management Directive determined that the primary effect observed with acute exposure to chloropicrin is sensory irritation, and the appropriate regulatory target level to restrict acute exposure to chloropicrin is 73 parts per billion or 0.073 parts per million averaged over an eight-hour period. As with other fumigants, a key element in mitigating exposure is establishing a buffer zone between a fumigated area and residents and bystanders.

The U.S. Environmental Protection Agency (U.S. EPA) employs buffer zones as one of the primary mitigation measures on its revised labels for chloropicrin products. For each particular use scenario, U.S. EPA presents a main buffer zone table containing buffer zones of maximum length and then gives buffer zones credits of up to 80% to reduce the size of a particular buffer zone. Those credits are applied directly to the buffer zone distance and not to the flux used to generate the buffer zone. U.S. EPA allows credits for the following factors: tarp type, organic matter, clay content, soil temperature, Symmetry System, potassium thiosulfate (KTS), and water seal applied over the tarp.

This document presents the approach DPR followed to develop buffer zones, using only flux data generated in the field. It describes the chloropicrin field data analysis performed to provide a basis for California buffer zone development. It discusses why DPR's methodology differs from that used by the U.S. EPA.

In addition, preliminary buffer zones are presented and the modeling system and methods used to develop them are described. Supporting information for the approach used to develop the chloropicrin buffer zones is also presented. The supporting information is drawn from analysis and modeling performed to develop other fumigant mitigation measures. These fumigants include methyl bromide, metam sodium, and methyl iodide. The topics in the supporting information are an analysis of the protection level of whole field versus maximum direction buffer zones (Appendix 6) and an analysis supporting the choice of weather data used to develop the chloropicrin buffer zones (Appendix 7).

Attachment 2 Description of Scientific Assumptions, Findings, and Conclusions to be Addressed by the Peer Reviewers

Reviewers are asked to determine whether the scientific work product is "based upon sound scientific knowledge, methods, and practices."

We request that you make this determination for each of the following issues. An explanatory statement is provided for each issue to focus the review.

For those work products which are not proposed rules, as is the case here, reviewers must measure the quality of the product with respect to the same exacting standard as if it was subject to Health and Safety Code 57004.

The following conclusions are based on information provided in DPR's document, "<u>Development of Chloropicrin Buffer Zones</u>."

1. DPR used data from 28 of the 47 fumigations available to determine buffer zones and correctly excluded, for scientific and policy reasons, data from 19 of the fumigations.

The U.S. Environmental Protection Agency (U.S. EPA) received data from pesticide registrants for 45 chloropicrin fumigations, which U.S. EPA used to revise labels for chloropicrin products as of December 2012 and develop mitigation measures, including buffer zones. DPR had access to two additional newer studies, for a total of 47 fumigations (see Appendix 1 in the "Development of Chloropicrin Buffer Zones").

As discussed on page 2 of the "Development of Chloropicrin Buffer Zones," DPR decided to exclude data from seven of the 47 fumigations for the reasons listed below (where *n* is the number of fumigations).

- Data did not did not meet the laboratory Quality Assurance/Quality Control standards for data submission and were, therefore, finally rejected after several additional submissions by the registrant (*n*=2).
- Data were submitted to U.S. EPA but not to DPR (*n*=1); since DPR did not have the data, DPR did not include them.
- Data were removed at the direction of DPR management (n=4).

Table 1 (page 4 of the "Development of Chloropicrin Buffer Zones") summarizes maximum flux in the chloropicrin database of 40 fumigations. As discussed on pages 2 through 5 in "Development of Chloropicrin Buffer Zones," DPR excluded 12 more studies for the following scientific reasons (where *n* is the number of fumigations).

- Symmetry Method application type across all tarp types because this method is not practiced in California (n=3).
- Metallized tarp type because the use of Metallized tarps is discouraged in California due to disposal issues (*n*=2).

• The VIF tarp type (*n*=1); strip application type (n=1); strip/deep application type (*n*=1); broadcast/deep application type (n=2); drip application type + TIF tarp type (*n*=1); and broadcast application type + TIF tarp type (*n*=1) were not conducted in enough combinations of applications and tarp types to allow inclusion in the statistical analysis.

Therefore, DPR used data from the remaining 28 fumigations for its evaluation (see Table 2 on page 5 of the "<u>Development of Chloropicrin Buffer Zones</u>").

2. DPR classified chloropicrin fumigation methods into only three groups, based on tarp type, and correctly excluded other tarp and application types.

Chloropicrin fumigation methods vary by application type (method of injection [tractor shank or drip irrigation], depth of injection [10 – 24 inches], field configuration [bedded or flat field]) and tarp type (untarped, poly tarp, totally impermeable film [TIF] tarp), and other parameters. DPR grouped fumigation methods by only tarp type because flux differences due to other fumigation methods were not statistically significant or it was not possible to perform a statistical analysis due to small sample size as discussed on pages 3 through 8 and shown in Figures 1, 2 and 3 in "Development of Chloropicrin Buffer Zones." Therefore, DPR used the following three tarp types to classify chloropicrin fumigations: untarped, Poly and TIF.

3. Peak flux sometimes occurred during the day and sometimes during the night, and DPR correctly and completely accounted for these time periods.

Peak flux for most fumigants and fumigation methods occur during daylight hours. Peak flux can occur at night in a few cases, but this is usually associated with particular fumigants and fumigation methods. Chloropicrin is the first fumigant evaluated by DPR that showed inconsistent times for peak flux, with no discernible pattern as discussed on pages 8 through 14 (see also Tables 3 and 4; and Figures 4-7) in "Development of Chloropicrin Buffer Zones." Peak flux at night results in much higher air concentrations and buffer zone distances compared to peak flux during the day due to differences in weather conditions. Because a consistent flux profile could not be determined, DPR modeled each of the 28 fumigations separately to determine buffer zone distances.

4. DPR concludes insufficient evidence exists to support most buffer zone reduction credits, contrary to the U.S. Environmental Protection Agency's (U.S. EPA's) conclusions.

Except for tarp type, DPR did not find evidence in the field study data to support the buffer zone credits awarded by U.S. EPA. U.S. EPA credits were developed using a mix of field results and soil column studies in the laboratory. Thus far, DPR has relied on field-generated data, not laboratory soil column studies, because the relationship between the laboratory results and field results are not quantified. U.S. EPA credits are for soil moisture at the time of application, soil temperature at the time of application, application of a water seal following application, application of reactive boundary layers such as potassium thiosulfate following application, organic content of the soil, and clay content of the soil. The following topics are analyzed and discussed in the "Development of Chloropicrin Buffer Zones" as shown below and were found not to be effective in changing flux data:

- Application of a reactive boundary layer following fumigant application, such as a KTS seal (pages 7 8 and Figure 3),
- Application of a water seal (page 8), and
- Soil moisture at time of application, Appendix 3

Such factors as soil temperature at time of application, organic content of soil and clay content of soil are not likely to be enforceable (see page 15 of the "Development of Chloropicrin Buffer Zones").

Based on these findings and conclusions, DPR does not use these U.S. EPA credits in its development of buffer zones.

The Big Picture

Reviewers are not limited to addressing only the specific topics presented above, and are asked to consider the following questions.

- (a) Are there any scientific issues not mentioned above that are part of the scientific basis of the proposed rule? If so, please comment on whether these are based on sound scientific knowledge, methods, and practices.
- (b) Taken as a whole, is the scientific portion of this proposal based upon sound scientific knowledge, methods, and practices?

Reviewers should also note that some proposed actions may rely on professional judgment where available scientific data are not as extensive as desired to support the statutory requirement for absolute scientific rigor. In these situations, the proposed course of action is favored over no action.

Attachment 3: List of Participants

For the sake of completeness, DPR has taken a special effort to identify everyone involved in the process. In addition to the staff who were involved (Section A) and those outside DPR involved (Sections B and C), this document was prepared using the available scientific literature and data (Section D).

Section A. California Department of Pesticide Regulation Staff

Chuck Andrews
Marylou Verder-Carlos, DVM, MPVM
David Duncan
Randy Segawa
Pamela Wofford
Terrell Barry, Ph.D.
Bruce Johnson, Ph.D.
Frank C. Spurlock, Ph.D.

Section B. Other Participants

David Sullivan – Sullivan Environment Consulting, Inc., Alexandria, Virginia Husein Ajwa – Department of Plant Sciences, University of California Davis, Salinas, California John R. Griffin – Exponent Inc., Menlo Park, California Richard Reiss – Exponent Inc., Menlo Park, California

Section C. University Scientists who Provided Comments during Public Comment Period on the Document Entitled "Chloropicrin Mitigation Proposal, May 15, 2013." Available at: http://www.cdpr.ca.gov/docs/whs/pdf/dpr_chloropicrin_mitigation_proposal_and_app_1-3.pdf

Mark Bolda – UC Cooperative Extension, Watsonville, CA

Jeffrey Jenkins – Department of Environmental & Molecular Toxicology, Oregon State University

David Doll – UC Cooperative Extension, Merced County, CA

Steven Fennimore – UC Cooperative Extension, Salinas, CA

Dale Hattis – Clark University, Worcester, MA

Section D. Bibliography

NOTE: The references highlighted in green are available only upon written request. Allow one month for delivery. To obtain copies of these documents, submit your request via e-mail to Jackie Rivers, DPR Staff Services Analyst, Registration Branch, at JRivers@cdpr.ca.gov. Be sure to include the CDPR data volume number in the list of references you provide. By law, she is required to contact each of the data owners to request their permission to release the data. Once she obtains all the permissions, she will ask the requestor to sign either a confidentiality form or a confirmation of status form. Then she will scan the documents and e-mail them to the requestor.

Ajwa, H. 2010. Chloropicrin flux rates for drip fumigation with PE and TIF tarps, water seal and KTS at Salinas, California in September 2007. Sullivan Environmental Consulting, Inc. 1900 Elkin Street, Suite 200, Alexandra, Virginia 22308. Laboratory Study ID HA2007-D. MRID 48087401. CDPR data volume 0199-0136.

Ajwa, H. and D. Sullivan. 2012. Soil fumigant emissions reduction using EVAL barrier resin film (VaporSafeTM) and evaluation of tarping duration needed to minimize fumigant total mass loss. Sullivan Environmental Consulting, Inc. 1900 Elkin Street, Suite 200, Alexandra, Virginia 22308. Laboratory Study ID HA2011A. CDPR data volume 50046-0198.

Ajwa, H. and D. Sullivan. 2010a. Monitoring of methyl bromide and chloropicrin field emissions from shank applications at shallow and deep injection depth. Sullivan Environmental Consulting, Inc. 1900 Elkin Street, Suite 200, Alexandra, Virginia 22308. Laboratory Study ID HA200901. MRID 48006001.

Ajwa, H. and D. Sullivan. 2010b. Monitoring 1, 3-dichloropropene and chloropicrin emission from solid-tarp shank injections at two sites near Fort Pierce, Florida. Sullivan Environmental Consulting, Inc. 1900 Elkin Street, Suite 200, Alexandra, Virginia 22308. Laboratory Study ID HA2009H. MRID 48085701.

Ajwa, H. and D. Sullivan. 2010c. Monitoring of methyl bromide and chloropicrin emission shank applications (bedded and broadcast) and a methyl bromide hot-gas application under totally impermeable film. Sullivan Environmental Consulting, Inc. 1900 Elkin Street, Suite 200, Alexandra, Virginia 22308. Laboratory Study ID HA201001. MRID 48107601. CDPR data volume 0199-0140.

Ajwa, H. and D. Sullivan. 2008. Monitoring of chloropicrin field emissions from shank applications at shallow and deep injection depths. Sullivan Environmental Consulting, Inc. 1900 Elkin Street, Suite 200, Alexandra, Virginia 22308. Laboratory Study ID HA200801. MRID 47576901

Ajwa, H., D. Sullivan and D. Chellemi. 2009a. Monitoring 1, 3-dichloropropene, chloropicrin and methyl isothiocyanate emissions from shank applications at three sites near Duette, Florida. Sullivan Environmental Consulting, Inc. 1900 Elkin Street, Suite 200, Alexandra, Virginia 22308. Laboratory Study ID 2009A. MRID 47813901.

Ajwa, H., D. Sullivan and D. Chellemi. 2009b. Monitoring chloropicrin, dimethyldisulfide, and methyl isothiocyanate emissions from shank applications at three sites near Tifton, Georgia. Sullivan Environmental Consulting, Inc. 1900 Elkin Street, Suite 200, Alexandra, Virginia 22308. Laboratory Study ID 2009B. MRID 48200001.

Baker, F.C. and T. Arndt. 2007a. Direct and indirect flux determination of iodomethane and chloropicrin under field conditions following tarped/raised bed/shallow shank injection application of MIDAS 50:50 in Dover, Florida. PTRL West Inc., 625-B Alfred Nobel Drive, Hercules, CA 94547. PTRL Project No. 1595W. MRID 47295202.

Baker, F.C. and T. Arndt. 2007b. Direct and indirect flux determination of iodomethane and chloropicrin under field conditions following tarped/raised bed/shallow shank injection application of MIDAS 50:50 in Bainbridge, GA. PTRL West Inc., 625-B Alfred Nobel Drive, Hercules, CA 94547. PTRL Project No. 1619W. MRID 47295203. CDPR data volume 52875-0129.

Baker, F.C. and T. Arndt. 2007c. Direct and indirect flux determination of iodomethane and chloropicrin under field conditions following tarped/raised bed/shallow shank injection application of MIDAS 50:50 in Hart, Michigan. PTRL West Inc., 625-B Alfred Nobel Drive, Hercules, CA 94547. PTRL Project No. 1646W. MRID 47295204. CDPR data volume 52875-0130.

Barry, T. 2005. Analysis of methyl bromide worksite plans, Memorandum to Randy Segawa, Senior Environmental Research Scientist, dated Feb 10, 2005. Department of Pesticide Regulation. California Environmental Protection Agency 95812-4015. Available at: http://em/localdocs/pubs/reviews/em0503.pdf>.

Barry, T. 2006. Development of methyl isothiocyanate buffer zones using the Probabilistic Exposure and Risk Model for Fumigants Version 2 (PERFUM2). Memorandum dated January 27, 2006 to Charles Andrews, Chief, Worker Health and Safety Branch. Environmental Monitoring Branch. Department of Pesticide Regulation. California Environmental Protection Agency. EM 06-05. Available at:

< http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/1776_andrews.pdf>.

Barry, T. 2007a. Development of additional methyl isothiocyanate buffer zones for the metam sodium mitigation proposal. Memorandum dated February 8, 2007 to Charles Andrews, Chief, Worker Health and Safety Branch. Environmental Monitoring Branch. Department of Pesticide Regulation. California Environmental Protection Agency. Available at:

http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/1884_Andrws_MITC.pdf.

Barry, T. 2007b. Resolving sources of differences in PERFUM methyl isothiocyanate buffer zones between Bakersfield and Ventura. Memorandum dated November 2, 2007 to Linda O'Connell, Senior Environmental Scientist (Supervisor), Worker Health and Safety Branch. Environmental Monitoring Branch. Department of Pesticide Regulation. California Environmental Protection Agency. [Included in the document under review as Appendix 7.]

Barry, T. 2013. Available soil moisture effect on maximum six hour flux. Memorandum dated February 12, 2013 to Randy Segawa, Environmental Program Manager I. Environmental Monitoring Branch. Department of Pesticide Regulation. California Environmental Protection Agency. [Included in the document under review as Appendix 6.]

Barry, T. and B. Johnson. 2005. Verification of probabilistic exposure and risk model for fumigants for 24-hour period maximum concentration calculations. Memorandum to Randy Segawa, Senior Environmental Research Scientist, dated September 19, 2005. Department of Pesticide Regulation, California Environmental Protection Agency. Sacramento, CA 95812-4015. [Hard copy included in this package.]

Barry, T. and B. Johnson. 2007. Analysis of the relationship between percentiles of the whole field buffer zone distribution and the maximum direction buffer zone distribution. Memorandum dated October 23, 2007 to Randy Segawa, Environmental Program Manager I. Environmental Monitoring Branch. Department of Pesticide Regulation. California Environmental Protection Agency. Available at: http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/1959_segawa.pdf>.

Barry, T., R. Segawa, and P. Wofford. 2004. Development of isothiocyanate buffer zones. Memorandum to John S. Sanders, Ph.D., dated February 24, 2004. California Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA 95812-4015. EM 04-09. [Hard copy included in this package.]

Beard, K.K., P.G. Murphy, D.D. Fontaine, and J.T. Weinberg. 1996. Monitoring of potential worker exposure, field flux and off-site air concentration during chloropicrin field application. Midland Industrial Hygiene Service Center. Health and Environmental Sciences. The Dow Chemical Company. Midland, Michigan 48674. Laboratory Project Study ID HEH160. MRID 44149201. CDPR data volume 0199-0072.

CMTF (Chloropicrin Manufacturing Task Force). 2011. Chloropicrin Manufacturers Task Force proposal for risk mitigation associated with potential chloropicrin exposures to residents and bystanders from agricultural use of pesticide products containing chloropicrin. Letter dated October 27, 2011 to Ms. Ann Hanger, Pesticide Registration Branch, California Department of Pesticide Regulation, 1001 I Street P.O. Box 4015, Sacramento, CA 95812-4015 from The Chloropicrin Manufacturer's Task Force, c/o Niklor Chemical Co., Inc., 1667 Purdy Avenue, Mojave, California 93501. [Hard copy included in this package.]

Cryer, Steven A. 2005. Predicting soil fumigant air concentrations under regional and diverse agronomic conditions. J. Environ. Qual. 34:2197:2207. [Hard copy included in this package.]

Freeman, Francis M. (Stenographer). 2004. Minutes from FIFRA Scientific Advisory Panel (SAP) Open Meeting August 24-25, 2004: A fumigant bystander exposure model review: probabilistic exposure and risk model for fumigants (PERFUM) using iodomethane as a case study. Tuesday, August 24, 2004, Volume I of II located at: Holiday Inn National Airport, 2650 Jefferson Davis Highway, Arlington, Virginia 22202. Available at:

http://www.epa.gov/scipoly/sap/meetings/2004/august1/august24transcript.pdf.

Gillis, M. and G. Smith. 2002. Chloropicrin emissions and offsite drift from tarped and non-tarped fields treated by a drip irrigation application method. Bolsa Research, 8770 Hwy 25. Hollister, CA 95023. MRID 47456001.

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Knuteson, J.A. and S.C. Dolder. 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. Global Environmental Chemistry Laboratory – Indianapolis Lab. Dow AgroSciences LLC. 9330 Zionsville Road, Indianapolis, Indiana 46268-1054. Laboratory Study ID 980070.01.

Reardon, C. 2013. Chloropicrin monitoring data used to determine buffer zones. Memorandum to David Duncan dated March 1, 2013. Department of Pesticide Regulation. California Environmental Protection Agency 95812-4015. [Hard copy included in this package.]

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Rotondardo, A. 2009. Direct flux determination of chloropicrin emissions from a drip, buried, nontarped application. PTRL West, Inc. 625-B Alfred Noble Drive, Hercules, California 94547. PRS08004. MRID 47679301. CDPR data volume 0199-0131.

Rotondardo, A. 2004. Monitoring of chloropicrin emissions from field and greenhouse drip irrigation applications, and implied worker inhalation exposure from applications of chloropicrin by shank injection, drip irrigation systems and at tree replant sites. Paragon Research Services, 332 W. Fountain Way, Fresno, CA 93705. Laboratory Study ID PRS02004. MRID 46420201,

Saxton, K. E., W. J. Rawls, J. S. Romberger, and R. I. Papendick. 1986. Estimating generalized soil water characteristics from texture. Soil Sci. Soc. Amer. J. 50(4):1031-1036. Available at: http://naldc.nal.usda.gov/download/35/PDF>.

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Segawa, R., T. Barry and B. Johnson. 2000. Recommendations for methyl bromide buffer zones for field fumigations. Memorandum to Dr. John S. Sanders, Chief, Environmental Monitoring Branch, dated January 21, 2000. Available at:

 $<\!\!\underline{http://www.cdpr.ca.gov/docs/specproj/tribal/recsformebrbuffzones.pdf}\!\!>\!.$

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State Water Resources Control Board

January 06, 2014

Mingxin Guo, Ph.D.
Professor of Soil and Water Sciences
Department of Agriculture and Natural Resources
Delaware State University
15 Baker Building
Dover, DE 19901

Dear Professor Guo.

PEER REVIEW OF THE DEPARTMENT OF PESTICIDE REGULATION'S METHODOLOGY TO DEVELOP BUFFER ZONES AND MITIGATION MEASURES FOR CHLOROPICRIN

I have been asked by the California Environmental Protection Agency's (Cal/EPA) Department of Pesticide Regulation (DPR) to continue managing the external scientific peer review of the subjects noted above. DPR will not communicate with the approved reviewers, such as yourself, nor know their identities, until I send the reviews to DPR.

My letter today is intended to initiate the next phase of the external review – the actual reviews themselves.

Included with this letter are the following key documents:

- 1. November 14, 2013 memorandum, from David Duncan to Gerald Bowes, "Request for an external peer review of the Department of Pesticide Regulation's methodology to develop buffer zones and mitigation measures for chloropicrin," which included the following attachments:
- -Attachment 1: Plain English summary of the proposal, "Development of Chloropicrin Buffer Zones"
- -Attachment 2: Description of scientific assumptions, findings, and conclusions to review
- -Attachment 3: List of participants
 - Section A. California Department of Pesticide Regulation Staff
 - Section B. Other Participants
 - Section C. Participants who provided comments during public comment period
 - Section D. Bibliography

CHARLES R. HOPPIN, CHAIRMAN | THOMAS HOWARD, EXECUTIVE DIRECTOR



2. Supporting documents for Attachment 1 and 3:

- A. Supporting documents for Attachment 1:
 - o DPR. 2013. Chloropicrin mitigation proposal
 - DPR. 2008. Memo to US EPA: Comments for Dockets EPA_HQ-OPP-2007-0350, EPA-HQ-OPP-2005-0128, EPA-HQ-OPP-2005, and EPA-HHQ-OPP-2005-0123
- B. Supporting documents (six hardcopy and seventeen on CD) for Attachment 3 Section D Bibliography, except those highlighted-see Section C below:
 - o Barry and Johnson. 2005
 - o Barry et al. 2004
 - o CMTF. 2011
 - o Cryer. 2005
 - o Johnson, 1999
 - o Reardon, 2013
- C. The highlighted references will be made available to reviewers on a separate CD when reviewers have signed the attached form entitled, "Acknowledgement of Data Handling Responsibilities" (DPR-REG-011), and returned it to me. You will be able to expedite this process by scanning your signed form and sending it to me by email. The original signed copy should then be sent by regular mail.

3. Proposal: "Development of Chloropicrin Buffer Zones," which includes:

- Memo from T. Barry to R. Segawa, dated March 20, 2013, transmitting entitled
 "Development of Chloropicrin Buffer Zones" (Major document to be reviewed)
- o Appendices 1 7

4. January 7, 2009 Supplement to the Cal/EPA Peer Review Guidelines.

Comments on the foregoing:

- 1. You have been sent the November 14, 2013 request memorandum during the solicitation process for reviewer candidates conducted by the University of California, Berkeley's Institute of the Environment.
- 2. <u>Attachment 2 to the request memorandum provides focus for the review.</u> I ask that you <u>address all topics, as expertise allows, in the order listed.</u>
- 3. The January 7, 2009 Supplement you received this earlier when I approved you as a reviewer. I am sending it again to make certain that you have it. In part, it provides guidance to ensure the review is kept confidential through its course. The Supplement notes reviewers are under no obligation to discuss their comments with third-parties after reviews have been submitted. We recommend they do not. All outside parties are provided opportunities to address a proposed regulatory action through a well-defined

regulatory process. Please direct enquiring parties to Mr. Duncan (<u>David.Duncan@cdpr.ca.gov</u>).

Questions about the review, or review material, should be for clarification, in writing – email is fine, and addressed to me. My responses will be in writing also. DPR should not be contacted.

Please send your reviews to me on February 28, 2014, not before. I will subsequently forward all reviews together to Mr. Duncan with reviewers' CVs. All this information will be posted at the appropriate DPR program web site.

Your acceptance of this review assignment is most appreciated.

Sincerely,

Gerald W. Bowes, Ph.D.

Manager, Cal/EPA Scientific Peer Review Program Office of Research, Planning and Performance State Water Resources Control Board 1001 "I" Street, MS-16B Sacramento, California 95814

Telephone: 916-341-5567 Facsimile: 916-341-5284

Email: GBowes@waterboards.ca.gov

Gerald W. Boyes

Attachments







State Water Resources Control Board

January 06, 2014

Glenn C. Miller, Ph.D.
Professor
Department of Natural Resources and Environmental Science
University of Nevada, Reno
1664 North Virginia Street
Reno, NV 89557

Dear Professor Miller,

PEER REVIEW OF THE DEPARTMENT OF PESTICIDE REGULATION'S METHODOLOGY TO DEVELOP BUFFER ZONES AND MITIGATION MEASURES FOR CHLOROPICRIN

I have been asked by the California Environmental Protection Agency's (Cal/EPA) Department of Pesticide Regulation (DPR) to continue managing the external scientific peer review of the subjects noted above. DPR will not communicate with the approved reviewers, such as yourself, nor know their identities, until I send the reviews to DPR.

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CHARLES R. HOPPIN, CHAIRMAN | THOMAS HOWARD, EXECUTIVE DIRECTOR



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Manager, Cal/EPA Scientific Peer Review Program Office of Research, Planning and Performance State Water Resources Control Board 1001 "I" Street, MS-16B Sacramento, California 95814

Telephone: 916-341-5567 Facsimile: 916-341-5284

Email: GBowes@waterboards.ca.gov

Gerald W. Boyes

Attachments







State Water Resources Control Board

January 06, 2014

James N. Seiber, Ph.D.
Editor-in-Chief, Journal of Agricultural and Food Chemistry
Department of Environmental Toxicology, Emeritus Professor
University of California, Davis
One Shields Avenue
Davis, CA 95616

Dear Professor Seiber.

PEER REVIEW OF THE DEPARTMENT OF PESTICIDE REGULATION'S METHODOLOGY TO DEVELOP BUFFER ZONES AND MITIGATION MEASURES FOR CHLOROPICRIN

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Gerald W. Bowes, Ph.D.

Manager, Cal/EPA Scientific Peer Review Program Office of Research, Planning and Performance State Water Resources Control Board 1001 "I" Street, MS-16B Sacramento, California 95814

Telephone: 916-341-5567 Facsimile: 916-341-5284

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Gerald W. Boyes

Attachments

Supplement to Cai/EPA External Scientific Peer Review Guidelines-"Exhibit F" in Cai/EPA Interagency Agreement with University of California Gerald W. Bowes, Ph.D.

Guidance to Staff:

- 1. <u>Revisions.</u> If you have revised any part of the initial request, please stamp "Revised" on each page where a change has been made, and the date of the change. Clearly describe the revision in the cover letter to reviewers, which transmits the material to be reviewed. The approved reviewers have seen your original request letter and attachments during the solicitation process, and must be made aware of changes.
- Documents requiring review. All important scientific underpinnings of a proposed science-based rule must be submitted for external peer review. The underpinnings would include all publications (including conference proceedings), reports, and raw data upon which the proposal is based. If there is a question about the value of a particular document, or parts of a document, I should be contacted.
- 3. <u>Documents not requiring review</u>. The Cai/EPA External Peer Review Guidelines note that there are circumstances where external peer review of supporting scientific documents is not required. An example would be "A particular work product that has been peer reviewed with a known record by a recognized expert or expert body." I would treat this allowance with caution. If you have any doubt about the quality of such external review, or of the reviewers' independence and objectivity, that work product-which could be a component of the proposal should be provided to the reviewers.
- 4. <u>Implementation review.</u> Publications which have a solid peer review record, such as a US EPA Criteria document, do not always include an implementation strategy. The Cai/EPA Guidelines require that the implementation of the scientific components of a proposal, or other initiative, must be submitted for external review.
- 5. <u>Identity of external reviewers.</u> External reviewers should not be informed about the identity of other external reviewers. Our goal has always been to solicit truly independent comments from each reviewer. Allowing the reviewers to know the identity of others sets up the potential for discussions between them that could devalue the independence of the reviews.
- 6. <u>Panel Formation.</u> Formation of reviewer panels is not appropriate. Panels can take on the appearance of scientific advisory committees and the external reviewers identified through the Cai/EPA process are not to be used as scientific advisors.
- 7. <u>Conference calls with reviewers.</u> Conference calls with one or more reviewers can be interpreted as seeking collaborative scientific input instead of critical review. Conference calls with reviewers are not allowed.

Guidance to Reviewers from Staff:

1. Discussion of review.

Reviewers are not allowed to discuss the proposal with individuals who participated in development of the proposal. These individuals are listed in Attachment 3 of the review request.

Discussions between staff and reviewers are not permitted. Reviewers may request clarification of certain aspects of the review process or the documents sent to them.

Clarification questions and responses must be in writing. Clarification questions about reviewers' comments by staff and others affiliated with the organization requesting the review, and the responses to them, also must be in writing. These communications will become part of the administrative record.

The organization requesting independent review should be careful that organization-reviewer communications do not become coilaboration, or are perceived by others to have become so. The reviewers are not technical advisors. As such, they would be considered participants in the development of the proposal, and would not be considered by the University of California as external reviewers for future revisions of this or related proposals. The statute requiring external review of science-based rules proposed by Cai/EPA organizations prohibits participants serving as peer reviewers.

2. Disclosure of reviewer Identity and release of review comments.

Confidentiality begins at the point a potential candidate is contacted by the University of California. Candidates who agree to complete the conflict of interest disclosure form should keep this matter confidential, and should not inform others about their possible role as reviewer.

Reviewer identity may be kept confidential until review comments are received by the organization that requested the review. After the comments are received, reviewer identity and comments must be made available to anyone requesting them.

Reviewers are under no obligation to disclose their identity to anyone enquiring. It is recommended reviewers keep their role confidential until after their reviews have been submitted.

Requests to reviewers by third parties to discuss comments.

After they have submitted their reviews, reviewers may be approached by third parties representing special interests, the press, or by colleagues. Reviewers are under no obligation to discuss their comments with them, and we recommend that they do not.

All outside parties are provided an opportunity to address a proposed regulatory action during the public comment period and at the Cai/EPA organization meeting where the proposal is considered for adoption. <u>Discussions outside these provided avenues for comment could seriously impede the orderly process for vetting the proposal under consideration.</u>

4. Reviewer contact information.

The reviewer's name and professional affiliation should accompany each review. Home address and other personal contact information are considered confidential and should not be part of the comment submittal.



Department of Pesticide Regulation



Brian R. Leahy

MEMORANDUM

TO: Gerald W. Bowes, Ph.D.

Manager, Cal/EPA Scientific Review Program Office of Research, Planning and Performance

State Water Resources Control Board

1001 I Street, MS 16B

Sacramento, California 95814

FROM: David Duncan, Environmental Program Manager

Environmental Monitoring Branch

916-445-3870

DATE: January 27, 2014

SUBJECT: REQUEST TO AMEND THE EXTERNAL PEER REVIEW FOR THE DEPARTMENT

OF PESTICIDE REGULATION'S METHODOLOGY TO DEVELOP BUFFER ZONES

Original Signed By

AND MITIGATION MEASURES FOR CHLOROPICRIN

In a memorandum dated November 14, 2013, the California Department of Pesticide Regulation (DPR) requested an external peer review of its methodology entitled "Development of Chloropicrin Buffer Zones." The methodology consists of analysis of field monitoring data performed to provide a basis for California buffer zone development. DPR will use the document to support future mitigation measures for chloropicrin, but regulations are not in development at this time. The request outlined four specific issues the peer reviewers should address. DPR would like to amend the peer review request to add a fifth specific issue described in the attached document.

If you have any questions regarding this request, please contact Randy Segawa, at 916-324-4137 or at <rsegawa@cdpr.ca.gov>. Thank you for your time and consideration of this request.

Attachments

cc: Randy Segawa, DPR Environmental Program Manager (w/Attachments)

Gerald W. Bowes January 27, 2014 Page 2

Amendment to Attachment 2 of DPR's request for a peer review of chloropicrin buffer zones, dated November 14, 2013. Description of Scientific Assumptions, Findings, and Conclusions to be Addressed by the Peer Reviewers

Conclusion 5. DPR utilized 1.25 m/s as the definition of a calm hour for wind speed and direction data from the California Irrigation Management Information System (CIMIS). Speeds at or below 1.25 m/s are considered calm hours for purposes of modeling and speeds above 1.25 are considered non-calm hours.

As described on page 27 of "Development of Chloropicrin Buffer Zones," DPR used CIMIS meteorological data for Ventura to determine the buffer zone distances. DPR's processing of the CIMIS data included a 1.25 m/s threshold for defining calm hours. The threshold value is based on the following information, assumptions, and analyses of the CIMIS data.

The minimum reported wind speed for CIMIS wind speed is 0.447 m/s. The CIMIS meteorological system uses Met024A wind direction sensor and Met014A wind speed sensor (CIMIS 2013). For both instruments the threshold is 0.447 m/s (1 mph). At low or zero wind speeds, the Met014A reports 0.447 m/s (Campbell Scientific 2011, 2012). Hourly wind speeds reported by the CIMIS stations are based on the average of 60 samples taken during the hour. Sixty samples are taken each hour for each CIMIS sensor (Eching and Moellenberndt 1998). Because the wind direction sensor (MET024A) has a threshold of 0.447 m/s, when an average wind speed is low, some fraction of the sixty wind direction measurements for the one hour average will reflect wind speeds below the threshold of the direction sensor and hence may reflect erroneous direction.

Scalar wind speeds follow a Weibull distribution. Deaves and Lines (1998, 1997) and Seguro and Lambert (2000) concluded that the Weibull distribution provides a good fit for wind speed over a wide range. To make a decision about which hourly average wind speeds and directions to use, a stochastic simulation was performed which fit CIMIS wind speed data to a Weibull distribution (Johnson 2001, Appendix 2). Based on simulation results, as average hourly wind speed decreased from 2.1 m/s to 0.447 m/s, the fraction of the sixty values below the instrument threshold increased from 0.13 to 0.40 (Figure Appendix 2.4, Johnson 2001). The increased fraction exhibited a break point at 1.25 m/s with more sharply increasing fraction to the left and less sharply decreasing fraction to the right (Figure Appendix 2.5, Johnson 2001). At this average speed, approximately 20% of the measurements are below the instrument threshold and approximately 80% are above the threshold.

REFERENCE

Campbell Scientific, Inc. 2012. Model 024A Met One Wind Direction Sensor Instruction Manual.

Campbell Scientific, Inc. 2011. Model 014A Met One Wind Speed Sensor Instruction Manual

CIMIS (California Irrigation Management Information System), Department of Water Resources, Office of Water Use Efficiency. http://www.cimis.water.ca.gov/cimis/infoStnSensorSpec.jsp

Deaves, D.M. and I.G. Lines. 1998. The nature and frequency of low wind speed conditions. Journal of Wind Engineering and Industrial Aerodynamics 73:1-29.

Deaves, D.M. and I.G. Lines. 1997. On the fitting of low mean windspeed data to the Weibull distribution. Journal of Wind Engineering and Industrial Aerodynamics 66:169-178.

Eching, Simon and David Moellenberndt. 1998. Technical Elements of CIMIS. The California Irrigation Management Information System. State of California, The Resources Agency, Department of Water Resources, Division of Planning and Local Assistance.

Johnson, Bruce. 2001. Appendix 2 from "Evaluating the effectiveness of methyl bromide soil buffer zones in maintaining acute exposures below a reference air concentration". State of California, Environmental Protection Agency, Department of Pesticide Regulation, Environmental Monitoring Branch, Environmental Hazards Assessment Program, 1001 I St. Sacramento CA 95812 EH00-10. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh0010.pdf

Seguro, J.V. and T.W. Lambert. 2000. Modern estimation of the parameters of the Weibull wind speed distribution for wind energy analysis. Journal of Wind Engineering and Industrial Aerodynamics 85:75-84.

CURRICULUM VITAE

MINGXIN GUO

Dept. of Agriculture and Natural Resources Delaware State University, Dover, DE 19901 Phone: (302) 857-6479; Fax: (302) 857-6455; E-mail: mguo@desu.edu

EDUCATION

Ph.D., Soil Science. Pennsylvania State University, 2001.

M.S., Environmental Chemistry. Chinese Academy of Sciences, 1995.

B.S., Environmental Soil Science. Beijing Agricultural University, 1990.

PROFESSIONAL EXPERIENCE

2004-present. Assistant Professor, Associate Professor, Professor of Soil and Water Sciences. Delaware State University, Dover.

2006-present. Adjunct Faculty. Department of Plant and Soil Sciences, University of Delaware, Newark, DE

2001-2004. Postdoctoral Researcher, Environmental Soil Chemistry. University of California, Riverside.

1995-1997. Research Scientist, Environmental Chemistry. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China.

TEACHING

Soil Science (Ag 208)

Soil and Water Management (NR 401)

Hydrology (NR 302)

Limnology (NR 313)

Biometrics (NR 321)

PROFESSIONAL SOCIETY MEMBERSHIPS

Soil Science Society of America (SSSA)

American Chemical Society (ACS)

HONORS AND RECOGNITIONS

Outstanding Associate Editor, Journal of Environmental Quality, 2012

Research Excellence Award, Delaware State University, 2013

SELECTED PUBLICATIONS (of 55)

- (1) Song, W. and M. Guo. 2013. Residual veterinary pharmaceuticals in animal manures and their environmental behaviors in soils. *In*: Z. He and H. Zhang (ed.) Applied Manure and Nutrient Chemistry for Sustainable Agriculture and Environment. Springer: New York, NY (In press).
- (2) Guo, M. 2013. Evolving bioretention techniques for urban stormwater treatment. Hydrol Current Res 4:e106. doi:10.4172/2157-7587.1000e106
- (3) Guo, M., Y. Shen, and Z. He. 2012. Poultry litter-based biochar: preparation, characterization, and utilization. p. 171–202. *In*: Z. He (ed.) Applied Research in Animal Manure Management: Challenges and Opportunities beyond the Adverse Environmental Impacts. Nova Science Publishers: Hauppauge, NY.
- (4) Guo, M., W. Song, and R. Kazda. 2012. Fertilizer value of lime-stabilized biosolids as a soil amendment. Agron. J. 104:1679–1686.
- (5) Song, W. and M. Guo. 2012. Quality variations of poultry litter biochars generated at different pyrolysis temperatures. J. Anal. Appl. Pyrolysis 94:138–145.
- (6) Guo, M. and W. Song. 2011. Converting poultry litter to activated carbon: optimal carbonization conditions and product adsorption for organics. Environ. Technol.32:1789–1798.
- (7) Guo, M., G. Qiu, and W. Song. 2010. Poultry litter-based activated carbon for removing heavy metal ions in water. Waste Manage. 30:308–315.
- (8) Guo, M. and S. Gao. 2009. Degradation of methyl iodide in soil: Effects of environmental factors. J. Environ. Qual. 38:513–519.
- (9) Wang, Q., M. Guo, and S.R. Yates. 2006. Degradation kinetics of manure-derived sulfadimethoxine in amended soil. J. Agric. Food Chem. 54:157–163.
- (10) Guo, M., S.R. Yates, S.K. Papiernik, and W. Zheng. 2005. Incompatibility of metam sodium with halogenated fumigants. Pest Manage. Sci. 61: 467–476.
- (11) Guo, M., W. Zheng, S.K. Papiernik, and S.R.Yates. 2004. Distribution and leaching of methyl iodide in soil following shank and drip application. J. Environ. Qual. 33:2149–2156.
- (12) Guo, M., S.K. Papiernik, W. Zheng and S.R. Yates. 2004. Effects of environmental factors on 1,3-dichloropropene hydrolysis in water and soil. J. Environ. Qual. 33:612–618.
- (13) Guo, M., S.R. Yates, W. Zheng and S.K. Papiernik. 2003. Leaching potential of persistent soil fumigant residues. Environ. Sci. Technol. 37:5181–5185.
- (14) Guo, M., S.K. Papiernik, W. Zheng and S.R. Yates. 2003. Formation and extraction of persistent fumigant residues in soils. Environ. Sci. Technol. 37:1844–1849.
- (15) Guo, M., J. Chorover, and R. Fox. 2001. Effects of spent mushroom substrate weathering on the chemistry of underlying soils. J. Environ. Qual. 30:2127–2134.

CURRICULUM VITAE

MILLER, GLENN C.

Address (Work) Department of Natural Resources and Environmental Sciences

Mail Stop 199 University of Nevada Reno, NV 89557

(775) 784-4108 FAX 775-784-4553 775-846-4516 (cell)

email: gcmiller@unr.edu

Education: University of California, Santa Barbara, CA B.S. Chemistry 1972

University of California, Davis, CA Ph.D. Agricultural Chemistry 1977

Employment:

Univ. of Nevada, Reno Aug-2009-present Professor, and Director of the

Graduate Program in Environmental

Sciences

2008-2009 On leave for 11 months serving as

Manager, Environmental Exposure Assessment, Valent USA Corporation,

Walnut Creek CA

2007-2008, 2010-2012 President UNR Nevada

Faculty Alliance

1995-2006 Director, Graduate Program in

Environmental Sciences

and Health

1998-2004 Director, Center for Environmental

Science and Engineering

1989- Professor

1983-89 Associate Professor 1979-83 Assistant Professor

1978-79 Lecturer

Environmental Protection Agency 1977-78 Research Chemist

Professional Societies:

American Chemical Society, Agrochemicals Division and Environmental Division American Association for the Advancement of Science Society of Environmental Toxicology and Chemistry Sigma Xi

Awards:

Thornton Peace Prize (1982)
Junior Faculty Research Award (1982)
UNR Foundation Professor (1991)
Conservationist of the Year, Nevada Wildlife Federation (1995)
College of Agriculture Researcher of the Year (1998)
Friend of the Lake Award, League to Save Lake Tahoe (2001)

Other Professional Activities

Environmental Protection Agency: Competitive Grants Review Panel 1985-1995

Environmental Protection Agency: Advisory Committee on Mining Waste 1991-1993

Environmental Protection Agency: Stakeholder Advisory Committee on Commodity Mercury 2007

Nevada Division of Environmental Protection: Technical Advisory Committee on the Carson River Superfund Site 1991-1994

American Chemical Society, Division of Environmental Chemistry: Chair of the Student Awards Committee 1988-1992

American Chemical Society, Division of Environmental Chemistry: Chair of the Awards Committee 1997-2002

UNR Environmental Studies Board: Chairman 1987-1991

UNR Environmental Science and Health Graduate Program: Director 1995-2006

Consultant to various public interest organizations, companies and law firms

Hydrology/Hydrogeology Graduate Faculty: Member 1989-present

Reviewer for numerous environmental chemistry journals

Co-owner and vice-president: Nevada Environmental Laboratories (Las Vegas and Reno) 1990-1999

Manager, Environmental Exposure Assessment, Valent USA Corporation 8/2008- 8/2009

Courses Taught

Humans and the Environment: Environment 100

Environmental Toxicology: NRES 432/632

Environmental Chemicals: Exposure, Transport and Fate: NRES 433/633

Analysis of Environmental Contaminants: NRES 430/630

Risk Assessment, NRES 793C

Global and Regional Issues in Environmental Science: NRES 467/667

Community and Conservation Service Activities

City of Reno, Charter Review Commission: Chairman 1990-93

Peavine Grade School PTA: Co-President 1990-1992

Sierra Club Mining Committee (national): Co-Chair 1989-1992 League to Save Lake Tahoe Board of Directors: 1986-1999

Mountain and Desert Research Fund: 1987-present

Dupont-Conoco Environmental Leadership Award in Mining Committee: 1989-1994

Nevada Interagency Reclamation Award Committee: 1990-1992 Washoe County School District Science Advisory Board: 1992-2000

Chairman, 1993-94

Earthwords: Board Member 1999-present

Tahoe Baikal Institute: Board Member 1998-present, Chair 2002-2003

Environmental Law Alliance Worldwide Board Member: 2000-present, Chair: 2009

Great Basin Mine Watch: Board Member 1994-present, Chair 2001-2006 Center for Science in Public Participation: Board Member 1998-present Great Basin Institute, Board Member 2000-present, Chair 2001-present United Nations Environmental Program Committee for Development of

a Code for Use of Cyanide in Mining: 2000-2002

Mining, Minerals and Sustainable Development, Assurance Group Committee Member, 2000-2002

National Research Council committee on Methyl Bromide: 1999-2001 National Research Council committee on Mining Technology: 2000-2002

National Research Council committee on USGS Mineral Resources Program, 2000-2003

US Environmental Protection Agency Committee on Management of Mercury Stores in the U.S. 2007

Research Interests: Remediation of mine waste contamination. Mining pit lake water quality. Fate and transport of organic compounds in soils and the atmosphere. Methods of remediation of gasoline contaminated soils; Photochemical transformation of organic contaminants on soil surfaces. Instrumental development of chromatographic systems. Development of arid lands biofuels

Grants Received: (1982-present)

- \$ 14,550 "Atmospheric Photolysis of Pesticides," A Junior Faculty Research Award from the UNR Research Advisory Board, 1982.
- \$ 3,000 "Photolysis of CGA-41065," CIBA GEIGY Corporation, 1982.
- \$ 4,000 "Chemotaxonomy of Sagebrush Using High Performance Liquid Chromatography," Intermountain Research Station USDA, 1984.
- \$ 83,000 "Analysis of Bovine Tissue for Chlorinated Hydrocarbons," Environmental Protection Agency, 1984-85.
- \$ 18,300 "Photooxidation of Sulfide Containing Pesticides on Soil Surfaces," Western Regional Pesticide Impact Assessment Program, 1984.
- \$ 2,500 "Identification of Sagebrush Taxa Based on Liquid Chromatographic Analyses of Phenolics" Research Advisory Board, 1986.
- \$235,500 "Factors Affecting the Photolysis of Dioxins on Soil Surfaces," U.S. Environmental Protection Agency, 1986-89.
- \$ 15,160 "Vapor Phase Photolysis of Phorate," American Cyanamid Corporation, 1987.
- \$ 2,500 "Identification of Sagebrush Taxa Based on Liquid Chromatographic Analyses of Phenolics," UNR Research Advisory Board, 1987.
- \$ 48,792 "Upgrading Municipal Wastewater Effluents for Urban Water Reuse through Phytochemical Oxidations: System Development and Operational Criteria," U.S. Geological Survey, State Water Research Institute Program (Co-P.I. with Richard Watts), 1986-88.
- \$ 17,200 "Vapor Phase Photolysis of Malathion," American Cyanamid, 1988.
- \$ 16,460 "Aging Groundwater: A comparison of the Fluorocarbon Method to the Tritium Method," U.S. Geological Survey, State Water Research Institute Program (Co-P.I. with K. Sertic), 1988-89. (Competitive Grant, State of Nevada) Terminated 6-89.
- \$206,000 "In Situ Treatment of Organic Hazardous Wastes in Surface Soils Using Fenton's Reagent." U.S. Environmental Protection Agency (Co-P.I. with Richard Watts), 1988-89. (Competitive Grant, national)
- \$ 23,200 "Evaporation of Gasoline from Soils," Nevada Division of Environmental Protection Co-P.I. with Susan Donaldson), (Contract).

\$ 50,000 "Photolysis of Pesticides on Soils," American Cyanamid Corporation (Unrestricted Grant, noncompetitive)

\$ 15,600 "Vapor Phase Photolysis of Diazinon and Methyl Parathion" Western Region Pesticide Impact Assessment Program (USDA) (competitive) 1989-90

\$ 30,000 "Interface for a Capillary electrophoresis Effluent and a Mass Spectrometer" Linear Corporation 1989-90. (Co P.I. with Murray Hackett) (contract)

\$ 15,000 "UV-Gas Chromatographic Dectector" Linear Corporation 1990. (Co P.I. with Murray Hackett) (Noncompetitive grant)

\$153,000 "Enhancement of Photodegradation of Pesticides in Soil by Transport Upward in Evaporating Water" (USGS Competitive) 1991-94

\$ 50,000 "Pit Water from Precious Metal Mines" U.S. Environmental Protection Agency, 1992-94

\$ 91,000 "Remediation of Acid Mine Drainage at Leviathon Mine" Lahontan Water Quality Control Board. (Contract, Co P.I. with Tom Wildman, Colorado School of Mines) 1992-94.

\$159,000 " Ecological Toxicology of Metam Sodium and it Derivatives in the Terrestrial and Riparian Environments of the Sacramento River" California Fish and Game, 1992-1995 (G.C. Miller project, part of a larger project with George Taylor at the Desert Research Institute)

\$43,092 "Atmospheric Transport and Deposition of Organophosphates and Other Pesticides as Input to Sierra Nevada Surface Waters" USDA-NRI. 1995-98. Co-P.I. with P.I. James N. Seiber. Task 2.

\$80,427 "Linked Techniques for Contaminant Removal from Soil in Arid/Semiarid Environments" Dept. of Energy. 1993-96. Co.P.I with James N. Seiber.

\$107,000 "Chemical Environmental Problems Associated with Mining" NIEHS 1993-96. Core B portion. This was a project of a larger Superfund Grant to UNR. James N. Seiber, P.I.

\$36,900 "Protocol for Evaluation of Pesticide Photodegradation" Dow-Elanco. 1995-97. (Contract)

\$45,000 "Photolysis of Pesticides" Dupont Chemical Company. 1995-98. Unrestricted gift to support ongoing research.

\$275,000 "Remediation of Acid Mine Drainage at the Leviathan Mine". Nevada Division of Environmental Protection. 1996-99

\$5000 "Evaluation of Limnology and Water Quality of a Porphyry-Copper Pit Mine Lake" Public Resource Associates 1996.

\$767,000 Geochemical, Biological and Economic Impacts of Arsenic and Related Oxyanions on a Mining-Impacted Watershed" NSF-EPA, 1997-01

\$46,000 "Remediation of Acid Mine Drainage at the Leviathan Mine". Lahontan Regional Water Quality Control Board, 2000-2001

\$30,000 "Use of Sulfate-Reducing Bioreactors to Remove Zinc in Mine Drainage" Placer Dome Corporation. 2000-2001

\$50,000 "Release of Gasoline Constituents from Marine Engines to Lake Tahoe" Lahontan Regional Water Quality Control Board, 1998-1999

\$70,000 "Impact of Marine Engine Exhaust on Pyramid Lake" U.S. Environmental Protection Agency, in cooperation with the Pyramid Lake Paiute Tribe. 2000-2001.

\$570,000 "An Environmental Assessment of the Impacts of Polycyclic Aromatic Hydrocarbons in Lake Tahoe and Donner Lake" California Regional Water Quality Control Board, Lahontan Region. 2001-2003.

\$126,000 "Operation of a Bioreactor at the Leviathan Mine" Contract with ARCO, 2001-2002

\$75,000 Trifluroacetic Acid in Antarctic Ice, National Science Foundation 2001-2004

\$190,500 "Mercury Deposition Associated with Mining, U.S. Environmental Protection Agency, 2002-2004

\$53,000 Passivation of Acid Generating Rock at the Golden Sunlight Mine, Placer Dome Corporation 2002-2003

\$520,000 "Operation of a Bioreactor at the Leviathan Mine" Contract with ARCO, 2003-2007

\$250,000 "Risk Assessment and Fate of Polyacrylamide and Acrylamide in Irrigation Canals and Receiving Water" A subcontract from the Desert Research Institute on a project from the U.S. Bureau of Reclamation. 2004-2008

\$55,000 Passivation of Acid Generating Rock, Freeport McMoran, 2009-2010

\$75,000 Biofuel crops on arid lands, Co-P.I. U.S. Department of Energy, 2010-2011

\$104,000 Development of a Good Neighbor Agreement for Mining, Newmont Mining Corporation 2012-2014

Publications:

- G.C. Miller and D.G. Crosby, "Photodecomposition of Sustar^R in Water." J. Agric. Food Chem. 26:1316 (1978).
- G.C. Miller and R.G. Zepp, "Effects of Suspended Sediments on Photolysis Rates of Dissolved Pollutants." Water Research 13:453 (1979).
- G.C., Miller, M.J. Miille, D.G. Crosby, S. Sontum and R.G. Zepp, "Photosolvolysis of 3,4-Dichloroaniline in Water: Evidence for an Aryl Cation Intermediate." Tetrahedron 35:1797 (1979).
- G.C. Miller and R.G. Zepp, "Photoreactivity of Pollutants Sorbed on Suspended Sediment." Environ. Sci. Technol. 13:860 (1979).
- G.C. Miller, R. Zisook and R.G. Zepp, "Photolysis of 3,4-Dichloroaniline in Natural Waters." J. Agric. Food Chem. 28:1053 (1980).
- G.C. Miller, R.G. Warren, K. Gohre and L. Hanks, "A Gas Chromatographic Method for Determining Strychnine Residues in Alfalfa." J. Assoc. Off. Anal. Chem. 65:901 (1982).
- G.C. Miller and W.W. Miller, Eds. "Effect of Sewage on the Truckee River." A symposium published by the University of Nevada, College of Agriculture (1982).

- G.C. Miller and R.G. Zepp, "Extrapolating Photolysis Rates from the Laboratory to the Environment." Residue Reviews 85:89 (1983).
- G.C. Miller and D.G. Crosby, "Pesticide Photoproducts: Generation and Significance." J. Clin. Toxicol. 19:707 (1983).
- G.C. Miller, W.W. Miller, J.W. Warren and L. Hanks, "Soil Sorption and Alfalfa Uptake of Strychnine Applied as an Agricultural Rodenticide." J. Environ. Quality 12:526 (1983).
- G.C. Miller and D.G. Crosby, "Photooxidation of 4-Chloroaniline and N-(4-Chlorophenyl)-Benzene-sulfonamide to Nitroso- and Nitro-Products." Chemosphere 12:1217-1227 (1983).
- K. Gohre and G.C. Miller, "Singlet Oxygen Generation on Soil Surfaces." J. Agri. and Food Chem. 31:1104-1108 (1983).
- R.G. Zepp, P.F. Schlotzhauer, M.S. Simmons, G.C. Miller, G.L. Baughman and N.L. Wolfe, "Dynamics of Pollutant Photoreactions in the Hydrosphere." J. of Fresenius Z. Anal. Chem. 319:119-125 (1984).
- K. Gohre and G.C. Miller, "Photochemical Generation of Singlet Oxygen on Non-transition Metal Surfaces." J. Chem. Soc. Faraday Trans. I 81:793-800 (1985).
- R.V. Tamma, G.C. Miller and R. Everett, "High-Performance Liquid Chromatographic Analysis of Coumarins and Flavonoids from Section Tridentatae of *Artemisia*." J. Chromatography 322:236-239 (1985).
- K. Gohre, R. Scholl and G.C. Miller, "Singlet Oxygen Reactions on Soil Surfaces." Environ. Sci. Technol. 20:934-938 (1986).
- K. Gohre and G.C. Miller, "Photooxidation of Thioether Pesticides on Soil Surfaces." J. Agric. Food Chem. 34:709-713 (1986).
- B.R. Smith, G.C. Miller, R.W. Mead and R.E.L. Taylor, "Biosynthesis of Asparagine and Taurine in the Freshwater Prawn, *Macrobrachium rosenbergii* (De Man)." Comp. Biochem. Physiol. 87B(4):827-831 (1987).
- B.R. Smith, G.C. Miller and R.W. Mead, "Taurine Tissue Concentrations and Salinity Effect on Taurine in the Freshwater Prawn *Macrobrachium rosenbergii* (De Man)." Comp. Biochem. Physiol. 87A(4):907-909 (1987).
- G.C. Miller and V. Hebert, "Environmental Photodecomposition of Pesticides." In: University of California publication Fate of Pesticides in the Environment (J.W. Biggar and J.N. Seiber, eds.) Chapt. 8, p. 75-86 (1987).
- G.C. Miller and R.G. Zepp, "2,3,7,8-Tetrachlorodibenzo-p-dioxin: Environmental Chemistry." In: Solving Hazardous Wastes Problems: Learning from Dioxins (J.H. Exner, ed.) American Chemical Society Symposium Series 338, Chapter 6, pp. 82-93 (1987).
- C.R. Blincoe, V.R. Bohman, G.C. Miller, R.L. Scholl, W.W. Sutton and L.R. Williams, "Excretion and Tissue Concentration of Pentachlorophenol Following Controlled Administration to Cattle." J. Animal Sci. 65 Supplement #1 (1987).

- G.C. Miller, V.R. Hebert and R.G. Zepp, "Chemistry and Photochemistry of Low-Volatility Organic Chemicals on Environmental Surfaces." Env. Sci. Tech. 21:1164-1167 (1987). V.R. Bohman, C.R. Blincoe, G.C. Miller, R.L. Scholl, W.W. Sutton and L.R. Williams, "Biological Monitoring Systems for Hazardous Waste Sites." EPA Final Report #CR 809 787 (1988).
- F.M. Wilt, G.C. Miller and R.L. Everett, "Monoterpene Concentrations of Litter and Soil of Singleleaf Pinyon Woodlands of the Western Great Basin." Great Basin Naturalist 48:228-231 (1988).
- K. Mongar and G.C. Miller, "Vapor Phase Photolysis of Trifluralin in an Outdoor Chamber." Chemosphere 17(11):2183-2188 (1988).
- G.C. Miller, V.R. Hebert and W.W. Miller, "Effects of Sunlight on Organic Contaminants at the Atmosphere Soil Interface." In: <u>Reactions and Movement of Organic Chemicals in Soils (B. Sawhney, ed.) SSSA Special Publication No. 22, pp. 99-110 (1989).</u>
- G.C. Miller, V.R. Hebert, M.J. Miille, R. Mitzel and R.G. Zepp, "Photolysis of Octachlorodibenzo-p-Dioxin on Soils: Production of 2,3,7,8-TCDD." Chemosphere 18(1-6):1265-1274 (1989).
- G.C. Miller, "Choosing an Analytical Lab" Nevada Waste Reporter Spring, 1989. (Publication of the Nevada Small Business Development Center).
- N.L. Wolfe, U. Mingelgrin and G.C. Miller, "Abiotic Transformation Processes in Water, Sediments and Soils." In: B. Spencer and H.H. Cheng, eds., <u>Pesticides and Other Toxic Organics in Soils</u>, Soil Science Society of America, pp. 103-168 (1990).
- S. Donaldson, G.C. Miller and W.W. Miller, "Extraction of Gasoline Constituents from Soil." J. Assn. Off. Anal. Chem. 73:306-311 (1990)
- V.R. Hebert and G.C. Miller, "Depth Dependence of Direct and Indirect Photolysis on Soil Surfaces." J. Agric. Food Chem. 38:913-918, (1990)
- J.M. Basey, S.H. Jenkins and G.C. Miller, "Food Selection by Beavers in Relation to Inducible Defenses of Quaking Aspens" Oikos 59:57-62 (1990).
- S. Donaldson, G. C. Miller, and W.W. Miller, "Volatilization of Gasoline Constituents from Soil. In: Proceedings of the Fourth National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, Las Vegas NV May, 1990.
- G.C. Miller, "Nevada's Environmental Commission: Changes Needed for the 1990's" in F. Ballister, Ed. <u>The Nevada Environmental Commission</u>, Published by Claremont College 1991.
- S. Kieatiwong, L.V. Nguyen, V.R. Hebert, M. Hackett, G.C. Miller, M.J. Miille and R. Mitzel, "Photolysis of Chlorinated Dioxins in Organic Solvents and on Soils." Env. Sci. Techol. 24:1575-1580, (1990).
- M. O. Theisen, G.C. Miller, C. Cripps, M. de Renobales and G.J. Blomquist, "Correlation of Carbaryl Uptake with Hydrocarbon Transport to the Cuticular Surface in the Cabbage Looper, <u>Trichlplusia Ni.</u> Pesticide Biochemistry and Physiology 40:111-116 (1991).
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- G.C. Miller, "Bringing Back the Land: Reclaiming Mining Disturbances" International Mine Waste Management, 1:1-5 (1991)

- F. M. Wilt and G.C. Miller, "Seasonal variation of coumarin and flavonoid concentrations in persistent leaves of wyoming big sagebrush (<u>Artemisia tridentata</u> ssp. <u>wyomingensis</u>: Asteraceae) Biochemical Systematics and Ecology, 20:53-67 (1992)
- F.M. Wilt, J.D. Geddes, R.V. Tamma, G.C. Miller and R.L. Everett, "Interspecific variation of phenolic concentrations in persistent leaves among six taxa from subgenus Tridentatae (McArthur) of <u>Artemisia</u> L. (Asteraceae)", Biochemical Systematics and Ecology, 20:41-52 (1992)
- S.G. Donaldson, G.C. Miller and W.W. Miller, "Remediation of Gasoline-Contaminated Soil by Passive volatilization" Journal of Environmental Quality, 21:94-102, (1992)
- R.J Watts, B.R. Smith and G.C. Miller, "Catalyzed Hydrogen Peroxide Treatment of Octachlorodibenzo-p-dioxin (OCDD) in Surface Soils", Chemosphere, 23:949-955 (1992)
- D. J. Bornhop, L. Hlousek, M. Hackett, H. Wang and G.C. Miller, "Remote Scanning Ultraviolet Detection for Capillary Gas Chromatography" Review of Scientific Instruments, 63:191-201 1992)
- B.W. Tyre, R.J. Watts and G.C. Miller, "Effect of Soil Organic Carbon on the Fenton's Reagent Treatment of Four Refractory Compounds" J. Environ. Qual. 20:832-838 (1992)
- S. Kieatiwong, G.C. Miller, "Photolysis of Aryl Ketones on Soil: The Effect of Vapor Transport" Environmental Chemistry and Toxicology, 11:173-179, (1992)
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- Miller, G.C. and S.G. Donaldson, "Factors Affecting Photolysis of Organic Compounds on Soils", in G.Helz, D.G. Crosby and R.G. Zepp, eds. *Surface and Aquatic Photochemistry*, Lewis Publishers (1993).
- Bird, D.A., W.B. Lyons, G.C. Miller, "An Assessment of Hydrogeochemical Computer Codes Applied to modeling Post-Mining Pit Water Geochemistry", in <u>Tailings and Mine Waste '94</u>, Proceedings of the first International Conference on Tailings and Mine Waste, '94. Fort Collins Colo. January 1994. p. 31-40.
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- R.J. Watts, S. Kong, M.P. Orr, G.C. Miller and B.J Henry, "Photocatalytic Inactivation of Coliform Bacteria and Viruses in Secondary Wastewater Effluent" Water Research 29:95-100. (1995)

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- G. A. Doyle, W. B. Lyons, G.C. Miller and S.G. Donaldson, "Oxyanion Concentrations in Eastern Sierra Nevada Rivers: 1. Selenium" Rivers: 1. Selenium" Applied Geochemistry, 10: 553-564 (1995).
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- S.G. Donaldson and G.C. Miller, "Transport and Photolysis of Pentachlorophenol in Soils Subject to Evaporating Water", J. Environ. Qual., 26:402-409 (1997)
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- V. R. Hebert and G.C. Miller, "Gas Phase Photolysis of Phorate", Chemosphere 36:2057-2066 (1998)
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- Miller, G.C., C. Hoonhout, W.W. Miller, M.M. Miller, "Geochemistry of Closed Heaps: A Rationale for Drainage Water Quality" in D. Kosich and G.C. Miller, eds, "Closure, Remediation and Management of Precious Metals Heap Leach Facilities", University of Nevada, (1999)
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- Hebert, V.R. and G.C. Miller, "Understanding the Tropospheric Transport and Fate of Agricultural Pesticides", Reviews of Environmental Contamination and Toxicology, 181:1-36 (2004)
- G. Jones and G. C. Miller, "Mercury and Modern Gold Mining in Nevada", a final project report submitted to the US.EPA. (2005)
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- C.E. Werkmeister, D.D. Malo, T.E. Schumacher, J.J. Doolittle, and G.C. Miller, "Testing Durability of Acid Rock Passivation to Root System Activity within Greenhouse Columns¹¹ R.I. Barnhisel (Ed.) Published by American Society of Mining and Reclamation, 3134 Montavesta Rd., Lexington, KY 40502. 2007.
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Honors and Accolades

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Kenneth Spencer Awardee, for Contributions in Agricultural and Food Chemistry, 2012

- American Chemical Society Fellow, 2010
- American Chemical Society, Agricultural and Food Chemistry Division Fellow, Fall, 2006.
- American Chemical Society International Award for Research in Agrochemicals, Fall, 1999
- •Chair, Risk Assessment Advisory Committee, California EPA, 1995-96
- •Member, National Academy of Sciences committees on Non-RCRA Hazardous Waste Classification, the Future Role of Pesticides in U.S. Agriculture, Pesticides in the Diet of Children and Infants, Risk Assessment for Hazardous Air Pollutants, 1988-2000
- •Steering Committee Member, WHO Joint IPCS/OECD Committee on Endocrine Disruptors, 1997-2002
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Current Research Interests

Agricultural and food chemistry; environmental sciences; transport and fate; chemistry of pesticides, industrial byproducts, and naturally occurring toxicants; ecological chemistry of plant-derived poisons; risk assessment for chemicals in food and the environment; trace organic analysis in water, soil, foods, and in the atmosphere; new methods for disposing of chemical, agricultural, and food wastes; new methods for controlling

agricultural pests; human exposure analysis; food protection; biobased products from renewable resources; environmental chemistry associated with biofuels

Biography

James N. Seiber, a native of Missouri, received his degrees in chemistry from Bellarmine College (Louisville, KY), Arizona State University (Tempe, AZ) and Utah State University (Logan, Utah). He has held positions as a research scientist at Dow Chemical Company (Midland MI and Walnut Creek, CA). He was a faculty member at the University of California Davis, Department of Environmental Toxicology where he served as Professor and Department Chair, and as Associate Dean for Research in the College of Agricultural and Environmental Sciences. He was founding director of the Center for Environmental Sciences and Engineering at the University of Nevada, Reno in 1992, where he initiated a multidisciplinary program of research and graduate education in Atmospheric Sciences, Hydrology, Conservation Biology, Environmental Health and Environmental Engineering.

He joined the U.S. Department of Agriculture's Agricultural Research Service in 1998 as Director of the Western Regional Research Center (WRRC) in Albany, CA. He oversaw scientists working in eight research units: Exotic and Invasive Weeds, Produce Safety and Health, Bioproduct Chemistry and Engineering, Processed Foods, Crop Improvement and Utilization, Plant Mycotoxins, Genomics and Gene Discovery, and Foodborne Contaminants. He was responsible for the development and implementation of food safety and biobased product initiatives at the WRRC. He also served as Acting Director of the ARS Western Human Nutrition Research Center and Southern Regional Research Center, and earlier in his career worked at the International Rice Research Center in the Philippines.

In 2009 he returned to academic life as interim Chair for the Department of Food Science and Technology at the University of California, Davis. He continues his affiliation at UC Davis as an emeritus Professor in the Department of Environmental Toxicology, teaching and conducting research on contaminants in foods and the environment.

Dr. Seiber continues to serve as Editor of the *Journal of Agricultural and Food Chemistry*. He is also a current member of the USDA-DOE Biomass Research and Development Technical Advisory Committee, the USDA-DOE Task Force on Agricultural Air Quality and Health, and the EPA Environmental Laboratory Advisory Board.

He has published over 250 book chapters and research manuscripts, and supervises dissertation research of Ph. D. and M.S. students.

11/27/2013

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DEPARTMENT OF AGRICULTURE AND NATURAL RESOURCES

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February 26, 2014

Review Comments on California Department of Pesticide Regulation (DPR)'s Methodology to Develop Buffer Zone and Mitigation Measures for Chloropicrin

The following documents from California DPR were intensively reviewed. Comments were based on information provided in these documents and other supporting documents.

- 1. Development of Chloropicrin Buffer Zones (March 26, 2013)
- 2. Development of Additional Methyl Isothiocyanate Buffer Zones for the Metam Sodium Mitigation Proposal (February 8, 2007)
- 3. Analysis of the Relationship between Percentiles of the Whole Field Buffer Zone Distribution and the Maximum Direction Buffer Zone Distribution (October 23, 2007)
- 4. Resolving Sources of Differences in PERFUM Methyl Isothiocyanate Buffer Zones Between Bakersfield and Ventura (November 2, 2007)
- 5. Request to Amend the External Peer Review for the Department of Pesticide Regulation's Methodology to Develop Buffer Zones and Mitigation Measures for Chloropicrin (January 27, 2014)

Chloropicrin has been identified by California Department of Pesticide Regulation (DPR) as a toxic air contaminant. The principal pathway for human exposure to this toxicant is inhalation after it is applied as a fumigant to control soil-borne pathogens. The primary acute exposure effect is sensory irritation. DPR, in agreement with the U.S. Environmental Protection Agency (EPA), determined a regulatory concentration of chloropicrin in ambient air at averagely 0.073 ppm (mg/L) over an 8-hr period to avoid acute exposure to this toxicant.

A buffer zone between a chloropicrin-fumigated area and nearby residents and bystanders is essential to control chloropicrin exposure. As many factors such as chloropicrin application rate, application method, field size, surface tarp type, soil characteristics, and weather conditions influence emissions and atmospheric diffusion of chloropicrin from treated fields, effective buffer zones (the distance away from the edge of the fumigated area to where the target 0.073 ppm chloropicrin air concentration reaches) vary in length with specific fumigation scenarios. Using primarily computer modeling with a modified CHAIN 2D solute movement model, EPA recommended minimum buffer zone lengths for particular chloropicrin uses, with assigning credits to decrease the required buffer zone length to the

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following factors: tarp type, soil organic matter content, clay content, soil temperature, Symmetry System fumigant injection, potassium thiosulfate spray, and water seal over tarp. Considering the particular fumigation practices, soil properties, and metrological conditions in California, DPR proposes a field flux-based approach to develop buffer zones for chloropicrin soil fumigation. The key points of the field flux-based approach are as follows. Review comments are made on each of the points.

1. DPR used data from 28 of the 47 fumigations available to determine buffer zones and correctly excluded, for scientific and policy reasons, data from 19 of the fumigations.

A database containing information of 47 field chloropicrin applications is currently available to DPR. These applications were conducted in different locations in CA, AZ, FL, GA, MI, and WA. The applications varied in chloropicrin application rate, application method, field acreage, surface tarp type, soil characteristics, and weather conditions, but most of them were measured for the maximum 6-hr chloropicrin flux (μ g/m² sec) from the treated area. Of the 47 applications, one did not contain data accessible for DPR, two were rejected by DPR as the flux sampling intervals during the first 48 hrs after fumigation started were not fixed (ranging from 3.5 to 11 hrs) and the data did not meet the laboratory quality assurance/control standards, and four were intentionally removed by DPR due to unreasonably high (outliers relative to other applications) maximum 6-hr flux values. It is appropriate to exclude these applications. DPR further excluded 12 applications that involved Symmetry Method fumigant injection, metallized tarp, VIF (virtually impermeable film) tarp, strip application, or strip/deep injection from the remaining 40 applications. The further exclusion is scientifically sound, as fumigation by Symmetry Method is not practiced in California, use of metalized tarp is discouraged, and VIF tarp and strip (/deep) applications were not conducted in adequate combinations of application type and tarp type to allow reliable statistical analysis.

Finally 28 applications were identified for statistical analysis to demonstrate the effects of fumigation method and tarp type on chloropicrin emissions (fluxes) from treated fields. If the applications were systematically designed, the sample size (e.g., $28 > 3 \times 3 \times 3$) is large enough to conduct ANOVA (analysis of variance).

2. DPR classified chloropicrin fumigation methods into only three groups, based on tarp type, and correctly excluded other tarp and application types.

The maximum 6-hr fumigant flux data of the selected 28 chloropicrin field applications were analyzed using unbalanced two-way ANOVA methods to evaluate the effects of application method (bed injection, solid field broadcast, drip/bed application) and tarp type (untarped, Poly tarp, TIF tarp) on emissions of chloropicrin from treated areas (Poly: polyethylene; TIF: totally impermeable film). The statistical results show that the effect of application method on the maximum 6-hr chloropicrin flux was insignificant or rather marginal, while the effect of tarp type was significant. Consequently, DPR classified chloropicrin fumigation methods into only three groups based the tarp type: untarped, Poly tarp, TIF tarp.

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The 28 chloropicrin field applications were correctly assigned to different treatment groups covering all possible combinations of application method (3 levels) and tarp type (3 levels). The two-way ANOVA statistical method itself is applicable to the data. However, those applications were not systematically designed for the purpose. Instead, the trials were conducted by different operators, in different locations, at different times, using different application rates, with different soils, and under different weather conditions. It is possible that the effects of other factors (e.g., soil moisture, temperature, and fumigation rate) that influence chloropicrin field emissions confounded effects of application method and tarp type, bringing forth the reliability concern on the ANOVA results. The reviewer suggests that **DPR use published research findings to provide additional support for the ANOVA inferences**.

The reviewer noticed that all maximum 6-hr chloropicrin flux data of the 28 applications with different application rates were normalized to the level for the 200 lb/ac application rate, assuming that chloropicrin flux is proportional to the application rate. This assumption may not stand. Scientific proof is needed to support the assumption.

The methods for applying fumigants to disinfect cropland soils can be broadly separated into two categories: broadcast (injection) application and drip application (chemigation) (Sprinkler application of metam sodium is excluded here). Broadcast application covers bed injection, strip injection, and solid (entire field) injection. Strip application of fumigants is practiced in California (e.g., in orchards) and therefore, cannot be neglected in the buffer zone development. Symmetry Method belongs to solid injection (termed as Broadcast in the present document). Deep injection (>18") is typically practiced as tree hole treatments without tarping (mechanical compaction of soil is used for sealing) and thus, can be distinguished in buffer zone development (so did in the present document). It is scientifically sound to classify fumigations into three groups based on the application methods: bed injection, broadcast (including both strip and solid injections), and drip application. When combining with surface tarping (untarped, Poly tarp, and TIF tarp), however, two more treatments should be included: strip Poly tarp and strip TIF tarp, since emissions of fumigants from these two scenarios will differ from solid Poly tarp and solid TIF tarp treatments, respectively. Further, VIF tarp can be treated as TIF tarp, as indicated by the similar chloropicrin emission reduction achievements of the two types of films in field applications (Table 1). In the meanwhile, LDPE (low density polyethylene), HDPE (high density polyethene), and SIF (semi-inpermeable film) films should be included in the "Poly tarp" group.

3. Peak flux sometimes occurred during the day and sometimes during the night, and DPR correctly and completely accounted for these time periods

A number of factors influence soil diffusion and subsequent atmospheric volatilization of fumigants from the fumigated field. The time for maximum 6-hr chloropicrin flux to occur after the fumigation starts depends on application method, tarp type, application depth, soil moisture, temperature, soil compaction, and etc. It is difficult, if not impossible, to predict the occurrence of maximum 6-hr chloropicrin flux at night or in the day, especially when the start time of fumigation

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in a day is not regulated. DPR analyzed the occurrence time of maximum 6-hr chloropicrin flux from the 28 field applications and found a random distribution of day-time and night-time occurrences regardless of the application start time and tarp type.

The day-time meteorological conditions are different from the night-time conditions. Air near the ground is generally more stable during the night time than during the day time. Diffusion of air toxicants from fumigated field to surrounding areas during day and night may follow varied patterns. It is essential to consider the occurrence time (day or night) of maximum 6/8-hr chloropicrin flux in developing effective buffer zones. DPR attempted to determine the sizes of buffer zones for chloropicrin fumigations resulting in specific maximum 6/8-hr chloropicrin fluxes by HYDRUS model simulations. A total of 1825 days (5 yr) of hourly weather data were used in modeling. For each day three 8-hr time intervals covering both day and night time occurrences of peak chloropicrin flux.

DPR further analyzed the 28 field chloropicrin applications and found that 95% of the maximum 6-hr fluxes occurred within 43 hours after the application was completed. Therefore, installation of a buffer zone for 48 hours after application is completed will provide adequate protection for residents and bystanders.

4. DPR concludes insufficient evidence exists to support most buffer zone reduction credits, contrary to the U.S. Environmental Protection Agency's (U.S. EPA's) conclusions.

U.S. EPA allocates credits for decreasing the required buffer zone length by 80% to the following factors: tarp type, soil organic matter content, clay content, soil temperature, Symmetry System fumigant injection, potassium thiosulfate (KTS) spray, and water seal over tarp. These EPA credit conclusions were based on research findings, as these factors do influence degradation, diffusion, and atmospheric emissions of field-applied fumigants including chloropicrin. It is confident that the chloropicrin flux profile will change if one of these creditable factors is manipulated, affecting the required length of an effective buffer zone.

Symmetry System fumigation is currently not practiced in California. Soil organic matter content and clay content vary over a large area (e.g., 40 ac) and with soil depth. Soil temperature further changes with season, weather, soil depth, and soil moisture content. Moreover, data of these soil properties are currently not available in California. It is not practical to extensively measure these parameters or to manipulate them in soil fumigation. Spraying KTS or applying water over Poly tarp or bed top is effective only in coincidence with maximum fumigant flux occurrence to reduce chloropicrin emissions. Since the time of maximum fumigant flux occurrence is largely unpredictable in individual soil fumigation events, application of KTS solution or water seal may merely result in wasting of water. Therefore, it is reasonable and acceptable that DPR does not give credits to the above soil factors, application method, and water/KTS spray in developing fumigation buffer zones.

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Only tarps should receive buffer zone credits. Using untarped fumigation as a reference, credits for Poly tarp and TIF tarp to decrease the buffer zone length can be estimated from their performance in reducing the maximum 6/8-hr chloropicrin flux. The credits have been incorporated in the methodology and are demonstrated in the proposed Percentile Buffer Zone Tables (Appendix 4) in the present document.

The statistical analyses conducted by DPR on the 28 field chloropicrin applications, however, cannot lead to conclusions that insufficient evidence exists to support most buffer zone reduction credits. Once again, these applications were not systematically (statistically) designed. The effects of many factors on the maximum 6-hr chloropicrin flux level were confounded and cannot be distinguished. Published research results should be visited for additional evidences. On the other hand, "certain actions may rely on professional judgment where available scientific data are not as extensive as desired to support the statutory requirement for absolute scientific rigor. In these situations, the proposed course of action is favored over no action."

5. DPR utilized 1.25 m/s as the definition of a clam hour for wind speed and direction data from the California Irrigation Management Information System (CIMIS). Speeds at or below 1.25 m/s are considered calm hours for purposes of modeling and speeds above 1.25 m/s are considered non-calm hours.

The meteorological data of Ventura, CA recorded by the California Irrigation Management Information System (CIMIS) were used by DPR to develop chloropicrin fumigation buffer zone regulations. The CIMIS data report on hourly-average wind speed from minute measurements. Due to the sensor sensitivity, wind speeds at or below 0.447 m/s (1 mph) were all treated as 0.447 m/s. Therefore, the CIMIS wind speed data overestimate the actual wind speeds. By stochastic simulations, DPR found that 13–40% (averagely 20%) of the minute measurements for the hourly average 4.7 mph wind speed at Merced, CA were actually at or below 0.447 m/s. At a 20% frequency of ≤1 mph wind, the hourly average wind speed is 2.8 mph (1.25 m/s).

In meteorology, calm air and light air are defined as with wind speed at 0-0.3 m/s and 0.3-1.5 m/s, respectively. If a 40% occurrence of \leq 1 mph wind in 60 minute-measurements is assumed, a calm air would demonstrate an hourly average wind speed at 0.5 m/s (= 0.3 + 0.447×40%) in the CIMIS data system. In many cases, however, light air (wind speed <1.5 m/s) is treated as calm air (EPA, 2011). Therefore, it is scientifically acceptable that DPR considers calm hours as the durations with average wind speeds at or below 1.25 m/s for modeling purposes.

EPA, 2011. AERMINUTE User's Instructions. Available at http://www.epa.gov/ttn/scram/models/aermod/aerminute_userguide_v11059_draft.pdf. Environmental Protection Agency: Washington, D.C.

Overall, the methodology used by DPR to develop buffer zone and mitigation measures for chloropicrin is scientifically sound and practically applicable. However, data from the selected 28 field chloropicrin applications are not adequate to support essential statistical analyses for concluding buffer



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Page 2. 95% of those applications

Page 2. The meteorological data were also uniform

Page 3. class F (highly stable)

Page 16. Table 8 title. Delete 100 from "represents 100 percentage of exceedances,"

Appendix 7: Resolving sources of differences in PERUM methyl isothiocyanate buffer zones between Bakersfield and Ventura

Page 3. Check the statement "In addition, the five year spans are different: 1999 through Ventura and 1995 through 1999 for Bakersfield." Indicated in the previous paragraph, Bakersfield data were from 1999 to 2003 and Ventura data from 1995 to 1999.

Appendix 2-4-4: Delete "maximum" from the phrase "the acceptable maximum level of"

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Review of

The California Department of Pesticide Regulation's Methodology to Develop Buffer Zones and Mitigation Measures for Chloropicrin

February 28, 2014

Submitted to

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Introduction

Chloropicrin has been used for several decades in California as a soil fumigant to control a variety of pathogenic organisms. As is the case for almost all pesticides, concerns have been expressed on use patterns due to the potential for human exposure. It is also a lachrymator and elicits a strong response from persons who are exposed to low concentrations of chloropicrin in air, either when used as a single fumigant, or in combination with other fumigants. The California Department of Pesticide Registration has prepared a document entitled "Chloropicrin Mitigation Proposal", which includes an appendix (4) entitled "Development of Chloropicrin Buffer Zones". I have been asked to review these documents and to provide comments on their scientific basis.

The request for review focused on whether the "scientific work product is based upon sound scientific knowledge, methods and practices". Because of the volatility of chloropicrin, the primary mode of loss from soil is volatilization, followed by transport in air to various receptors. In order to protect human health, the concentration of chloropicrin in air should be sufficiently low to minimize or eliminate potential health impacts. Thus, to the extent possible, volatilization of chloropicrin from treated fields should be minimized, and buffer zones created to allow dilution of the chloropicrin to below the reference dose as it migrates away from the application site. Understanding the volatilization of chloropicrin downwind from emissions from soils is straightforward, in that emissions should be measured under a variety of conditions and, using standard air movement and dilution models, the downwind concentrations can be estimated, and the buffer zones established to minimize exposure.

In practice, however, this is a very challenging effort, due to the uncertainty of each factor that affects volatilization, particularly the rate of emissions from soils, even when using a variety of techniques for minimizing the loss. Wind velocity, soil moisture, soil type, organic content of the soils, particle size distribution, temperature, type of tarping (if any), application rate, size and frequency of application, transformation of the fumigant in soil and air, among other factors all can affect the concentrations to which people are exposed. An additional factor that is difficult to include in the buffer zone estimates is the expertise and care of the applicator during the application. In addition, substantial differences in exposure effects and sensitivity to chloropicrin are evident. Each of these factors requires an intensive review of all of the data by regulators and the public (including the industry) to allow the best decisions on how to protect the public from the potential health effects.

The review requested that I make a determination for each of the following issues, using the specific requests and numbering system of Attachment 2 of the request for review.

1. DPR used data from 28 of the 47 fumigations available to determine buffer zones and correctly excluded, for scientific and policy reasons, data from 19 of the fumigations.

Exclusion of data from a decision-making process is always an important concern, particularly when the variability of data from field studies can be substantial. In this case, improper elimination of data sets may inappropriately influence the buffer zone decisions. However, based on the documents reviewed, excluding certain studies on chloropicrin use appears to be well justified.

Of the data base of 47 chloropicrin studies, 7 were initially removed. The 47 studies included the 45 studies utilized by the EPA for their buffer zone decisions, plus two additional studies that were conducted more recently. Four of the studies were excluded by DPR management, perhaps, in part, because they were conducted in Arizona (although no comment was presented as to the technical reasons why they were excluded); the DPR staff excluded one study with two applications (also in Arizona), based on data deficiencies; and one study used by the EPA was not received by the DPR, leaving 40 studies that received additional screening by the DPR. A letter from Ann Hanger, representing the Chloropicrin Manufacturers' Association Task Force appears to agree with exclusion of the Arizona studies, since they appear to have *not* been conducted in accordance with Good Agricultural Practices, and the methods used for those applications of chloropicrin would not be allowed, based on current label requirements.

Of the 40 remaining studies received by the DPR, 12 additional studies were also excluded. The reasons for exclusion of the 12 additional studies were briefly described and consisted primarily of differences in methodology for application of chloropicrin. The studies that were removed included the Symmetry Method (?) and metallized (20% credit tarp credit), which are either not practiced in California or discouraged (metalized) due to disposal issues. The remaining excluded studies included VIF tarp use, strip and deep injection applications, which had not been conducted with sufficient repetitions to allow inclusion in the statistical analysis. Of this group of 12, two additional studies were excluded due to complications from other applications nearby or problems with maximum flux estimates. The three major application methods examined intensively, included untarped, poly tarped or TIF tarped application methods. Thus, the exclusion of the 19 total studies appears well-justified.

The DPR analysis of the use of the 28 remaining studies is presented well and utilized valid statistical methods to establish that the three application methods used for establishment of the buffer studies were indeed appropriate. These studies are all conducted under Good Laboratory Practices (GLP) and are credible studies, although the variability in the results is fairly large, which is not unexpected due to the differences in field sites and site specific conditions. The exclusion of the 19 studies, as discussed above is reasonable, and the rational for exclusion of those studies is generally stated clearly, except, perhaps for the excluded Arizona studies.

2. DPR classified chloropicrin fumigation methods into only three groups, based on tarp type, and correctly excluded other tarp and application type.

Creation of buffer zones for chloropicrin applications utilized three groups, including untarped, poly tarped and TIF tarped methods. However, a variety of variations of these three application types were utilized in the 28 studies. The March 26, 2013 memo from Randy Segawa, discusses the variation in methods and concludes that there was no (or marginal) statistically significant differences in these application methods, and, of these studies, the differences were small and did not provide a basis for separation of these application methods into a larger number of different application methods. Examples of the differences were deep injection with tarping and use of potassium thiosulfate as a method for rapidly degrading chloropicrin. Due to the lack of repetition or the lack of differences, only the three major application methods were examined for creation of buffer zones. As the Segawa memo indicates, further studies on these variations in application methods may, in the future, allow additional application methods to have different buffer zones. At present, based on the available data, I agree with the DPR that the data are sufficient to justify only the three methods of application for establishment of buffer zones. The use of only three application methods also simplifies the enforcement of regulation, and reduces opportunities of unintentional or intentional misapplication.

2. Peak flux sometimes occurred during the day and sometimes during the night, and the DPR correctly and completely accounted for these time periods.

I was initially surprised by the lack of differences between nighttime and daytime emission rates. Higher temperatures during the day are expected to increase volatilization rates, but on further consideration, dry surface soils can retard the emissions though sorption of chloropicrin on those very dry near-surface soils. During night, when temperatures are cool, the humidity in the cells and movement of water towards the surface can hydrate the soils and decrease sorption of the chloropicrin on the soils. But, the observation of no statistically significant difference in maximum 6-hr flux rates between day and night is, at the very least, interesting. I note that in Table 3, there were more daytime maximum flux rates- in the case of the 15 studies of the poly tarped applications, 10 applications produced maximum daytime emissions, while only 5 produced maximum night time emissions.

The Segawa March26, 2013 memo appropriately notes that "... night meteorological conditions are more stable relative to day conditions. The same flux value will produce higher air concentrations at night. The buffer zone development must take into account whether the maximum 6-hour flux occurred at night or day". I agree strongly. In other efforts on estimating risk of methyl bromide to people living nearby, a review committee noted that the greatest expected exposure would be during very calm (perhaps with an inversion) conditions where the air mass would be moving very slowly, and produce the highest exposure concentrations. The observation of highest 6-hour

emission rates following some applications during nighttime provides additional support for establishing buffer zones based on calm nighttime conditions, where both emission rates and low dilution can maximize exposure.

The DPR appropriately considered this important variable in buffer zone creation.

4. DPR concludes insufficient evidence exists to support most buffer zone reduction credits, contrary to the U.S. Environmental Protection Agency's (U.S. EPA's) conclusion.

Although I did not extensively review the rationale for the U.S. EPA's buffer zone credits, the Segawa March 26, 2013 memo is persuasive. The use of buffer zone credits must consider all of the available valid data, but should not use data that is equivocal or meager. Indeed, certain additional practices may reduce emission rates. If practices can be used to reliably reduce emission rates, those practices should be encouraged. For example, the chemistry of using potassium thiosulfate (KTS) as a method for establishment of a barrier for chloropicrin emissions via reactions that destroy chloropicrin, has shown success under laboratory conditions, and makes chemical sense. The data presented in the Segawa March 26, 2013 memo (Fig. 3) supports the notion that KTS deserves some additional attention, but the field data are scant in this regard and additional studies are required to confirm this interesting chemical results. I agree that the data are presently insufficient to provide buffer credits at this time. A similar argument can be made for deeper injection depths. The data (Fig. 2) suggest that deep injections may decrease emission rates, but the number of studies available is insufficient to make a regulatory decision that buffer credits should be provided for those deep injections.

Additionally, enforcement of buffer zones is assisted by having relatively uncomplicated requirements, and use of the three application methods is very straightforward, and more easily enforced. Complicating the use of buffer zones by use of water content, soil temperature, soil type, etc. is arguably not in the best interests for enforcement and protection of persons living near treated fields.

I also agree with the DPR's use of only field based studies for establishing buffer zone. Laboratory data developed on emission factors for chloropicrin are critical for understanding the factors that control emission from soils. These factors can be carefully controlled so that the factors of temperature, soil type, organic content, water content, etc. can be evaluated. However, extrapolation of those data to the field, particularly when human exposures are being derived, are sufficiently unreliable that regulatory decisions should be made primarily, if not exclusively, with field-obtained data. I agree with the DPR that emission factors are best determined on a field scale level. Although these field studies are expensive, they provide emission factors that are more reliable for estimating human exposure and ultimately to protect human health.

Additional comments:

- 1. Some additional discussion (page 1 of the Chloropicrin Mitigation Proposal) of the environmental fate of chloropicrin would have been helpful, particularly as it relates to reduction in concentrations of chloropicrin in soils or air. Fumigants such as methyl bromide and metam sodium (and MITC) react in a reasonably rapid manner with soils. The volatile MITC is both transformed by hydroxyl radical and direct photolysis in air, although the rates are sufficiently slow ($t_{1/2}$ several hours) that they are unlikely to substantially affect exposure concentrations during night or during sunlight hours. Recent work by Vera and coworkers (Vera, et al., "Photolysis of Trichloronitromethane (Chloropicrin) under Atmospheric Conditions" Vol. 224 (2010)) indicates that the direct photolysis half-life in air is 5-7 hours, which also renders this conversion rate slow, compared to the exposure periods of concern. The time that it takes for emitted chloropicrin from the soil to migrate to the exposed person is short, compared to the photolysis period. Some comments could have been presented on the reactions of chloropicrin in soils, where both microbial and abiotic processes are involved, with first order half-lives relatively short, and on the order of <1 to 8 days (publications too numerous to include here, but the work of Gan and coworkers and UC Riverside is particularly noted.) These data lend increased confidence that the tarp cutting period limitations are appropriate.
- 2. Some additional discussion on the variety of tarps used during chloropicrin application would have been helpful. While I understand that California standards exist for the use of the various tarps, the variability in the degree of penetration of chloropicrin through these tarps is a question that is a bit vexing. The Segawa memorandum of March 26, 2013 on the "Development of Chloropicrin Buffer Zones" shows clearly that statistically significant (and visually obvious) differences in cloropicrin emissions exist between tarped, poly tarped and TIF tarped fields. It is less clear whether major differences exist between the variety of polyethylene tarps used during application. The type of tarp used in the application is presented in the provided studies, but review of those data are beyond the scope of this review. This concern is not major, however, since the buffer zones created by way of use of emission rates of chloropicrin and the two major tarp types is sound and justified.
- 3. Data on concentrations of chloropicrin in regard to the reference/regulatory exposure limit of 73 ppb would have been helpful, rather than just emission rates. While these are well correlated for exposure for situations where maximum direction models are utilized, having actual field data compared to modeled data would have been interesting and useful. For the 28 field studies utilized in the establishment of buffer zones, how did the measured values compare to the modeled values.
- 4. I am less comfortable evaluating the quality of the air modeling model PERFUM, other than a recognition that these models are widely utilized and well established. The

- concept of using the maximum direction distribution, as proposed does make sense, in that it is more conservative and considers individual exposures.
- 5. There appears to no significant disagreements with the U.S EPA on the basic toxicology and reference dose for chloropicrin. While there is disagreement on how the exposure models can be used, and the appropriate models, the differences really are not substantial, and both the federal and state agencies are in general agreement on how to reduce exposure. The buffer zones used for California application of chloropicrin are more conservative than those of the U.S. EPA, but appear to be generally consistent within the uncertainty of predicting the exposures that will occur following individual chloropicrin applications. The perhaps largest disagreement with the EPA buffer zones is the determination by the DPR that certain application techniques do not merit buffer zone credits. That decision appears well supported, either by the lack of conclusive data or by the lack of statistically significant reductions in chloropicrin emissions using those practices.

Concluding Comments- The Big Picture

The scientific validity of the California DPR's methods for determining the variables for establishing buffer sounds appears sound. The combination of using validated GLP studies under a variety of conditions for chloropicrin emissions rates, coupled with established air quality models, is a straightforward method for the establishment of buffer zones to mitigate exposures to chloropicrin. The provided documents are based on a reasonably large data set, and the decision to use three emission scenarios (untarped, poly tarped and TIF tarped systems) is well-defended and appropriate. While chloropicrin exposures are unlikely to be eliminated entirely, the concentrations to which people will be exposed (at a 95% confidence) are low and these new buffer zones promise to further mitigate the potential impacts to human health.

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2/28/14

Peer Review of DPR Methodology to Develop Buffer Zones and Mitigation Measures for Chloropicrin

Original signed by

James N. Seiber, Professor Emeritus

General comments

DPR staff are commended for doing an exhaustive evaluation of possibilities for developing buffer zones for chloropicrin. Much of the evaluation depends on state-of-the-art models. The following comments are meant to aid in interpretation, clarification, and avoiding possible pitfalls. They are not meant to detract from the overall value of the work performed.

Some results do not include adequate statements or estimates of uncertainty. See comments below on proposed buffer zone distances. In general when a single number is presented in a table, or for linear graphical correlations, some estimate should be given of the degree of precision associated with that number or correlation.

Some data was removed from consideration at the request of DPR management. The rationale was not explained in the document although it was noted (p 2) these studies were conducted in Arizona. Is there a scientific reason for excluding these studies?

Six hour flux was used without adjustment to 8 hour work day. Not clear why this was considered acceptable in the report.

Water level in soil can potentially affect flux, but neither the fumigant—to-water ratio, nor the percent water in soil was given eg in Table 1 or discussed adequately in this section of the report. The effect of water on flux should be commented upon, particularly for the drip application method. [I later saw the commentary on effect of available water moisture on six hour flux, in the Feb 12, 2013 memo from Barry to Segawa. This analysis indicates water moisture did not correlate with flux. This analysis should be referenced in the section of the main report which contains Table 1, even though it appears to run counter to what is the case for soil applied pesticides in general, based on prior studies]

The results from the Hydrus model are not available for inclusion, but it appears that they are needed to make this analysis complete.

For a key application variable, injection depth, there was insufficient data to evaluate.

This is a shortcoming of the report. See p 6. In most previous studies of soil-applied pesticides of all types depth of placement is a key variable. (see references by Spencer, Taylor, Glotfelty as examples)

KTS barriers have shown promise from lab, chamber, and field studies. Results should be presented, perhaps in a footnote or anecdotal statement in order to complete the options discussed in the report, even though the data are not as robust as desired. see p 7

Would like to see the effect of soil temperature, soil moisture and wind speed as variables p 13 states that some variables, such as soil temp, are not enforceable. Not clear why this is so, or why it should affect a discussion of the results in this report.

Fig 8, p 18 shows some periodicity in max flux. But this is not commented on. Is there a factor, such as max sunlight intensity hitting the tarp, at work here?

What conclusions are we to draw from Fig 10, p 19? This data set is hard to decipher, and hard to interpret. Every Figure and Table should be discussed in the report. If there is no discussion, these figures or tables with no discussion should be dropped, or placed in an appendix.

Flux from tarp cutting after application will depend on the concentration of chloropicrin under the tarp, ie between surface of soil and tarp. A better measure of this factor as a potential variable might be head-space analysis under the tarp, rather than full flux determination. P 22 and ff. Was this considered?

The whole field vs maximum direction section (p25 ff) is hard to follow. Suggest a rewrite to simplify, and bring out the main points for the reader.

From the data in section 6, p 27 ff, it appears that the Ventura data gives the more health protective buffer zone and should be the correct set to choose. Is it possible that this could be overturned by site specific wind data? This might be a possibility for those applicators who wish to go to the trouble of measuring wind speed and direction for 'their' site.

Appendix 4 would benefit from a legend entitled 'how this table is meant to be used'. This starts to come through after a couple of perusals, but be better to make it clear in the legend. Is there any latitude in enforcement of the buffer distance in feet, eg +/- 5 %?

Screening condition buffer zones, used in the absence of the more complete documentation of buffer zones given in this report, are presented in the Feb 8 memo, from Barry to Andrews. First comment, these buffer zones are given in meters where the ones in the updated report are in feet—a minor inconsistency. To put the screening method into context of the report, it would be good to have comments on the screening method, and the degree of protectiveness it has provided, in the discussion section of the main report. In other words, cross referencing these appendix items back to the appropriate section of the full report would be helpful. The use of ISCST3 model is once again affirmed as the appropriate model—in recognition of the scientific underpinnings of ISCST3.

Comparison between FEMS and PERFUM2 models (page 4) is important, but I wonder if it could be simplified for sake of this report. This gets into a level of detail that somewhat confuses the main points of the report. Why not standardize on just one of the two models?

Discussion of the whole field method and maximum direction methods concludes (p9, Oct 23, 2007 memo) with statement that the whole field method does not take into account population centers which, in California, are likely to be encountered. This seems to be a serious drawback. Has this been rectified in the methodology evaluated in the updated report?

Appendix B, p 26, again gets into considerable detail on modifications of PERFUM2 to obtain daily spoke-specific buffer information. The section does not contain enough information on why this is being done, or how it will aid

in protecting health of persons downwind from the applications of metam. In other words, the question 'so what' comes up often and is difficult to answer in spite of the volumes of data presented. Suggest these technical sections be revised and simplified, or preceded with an executive summary that puts the information into perspective. Same comment for appendices DEF, although Figure F1 is useful and might be highlighted in some way.

Appendix 7 (Nov 2, 2007 memo) demonstrates that the choice of weather data affects the results of buffer zone calculations in a pronounced way, with Ventura data giving buffer zones about twice those using Bakersfield data. Is there a recommendation in the report as to which should be used? Can we presume that the more protective buffer zones, calculated from Ventura data, are to be used, or is this an option depending on where the fields in question are located (ie coastal vs Central Valley)?

It is understandable that portions of this report will be amended when more recent data, (eg availability of Hydrus model) is forthcoming. It would be good to put this sort of information in a concluding or overview section.

Answers to Determination of whether the scientific work product is "based upon sound scientific knowledge, methods and practices for each of Four Points posed on pp 4 and 5 of Attachment 2"

1. DPR used data from 28 of the 47 fumigations available to determine buffer zones, and correctly excluded, for scientific and policy reasons, data from 19 of the fumigations.

In most cases the reason for exclusion was clearly given and follows sound reasoning. An exception is for 4 fumigations made in Arizona for which no clear reasons were apparent to this reviewer, except that they were removed at the request of DPR management. Not clear what scientific reason existed for excluding these data.

It would also help to have better reasoning for excluding the data from 3 Symmetry method applications, than the stated reason that the Symmetry method is not practiced in California. After reading up some on the symmetry based method, I view it as a reasonable alternative application type that may affect flux and other parameters, and I wondered how it can be categorically stated that it is not practiced in CA with an implication that it will never be practiced in CA. This seemed arbitrary.

- 2. DPR classified chloropicrin fumigation methods into to only 3 groups, based on tarp type, and correctly excluded other tarp and application types. The reasons for excluding other types were stated as due to lack of statistical significance or too small of sample size (both valid reasons from my viewpoint). This left only 3 tarp types as the basis for comparisons—untarped, poly, and TIF. These choices appear to this reviewer to agree with the primary variable faced by applicators, although several others—depth of incorporation, soil temp, depth of injection, tarp cutting time, soil moisture content—are considered by applicators as well. See my comment on water level in soil in my summary General Comments. For some of these there are good data in the literature from model chamber and related lab studies, See references in Woodrow et al A correlation to estimate emission rates for soil-applied fumigants, J. Agricultural and Food Chemistry, 59, 939-943 (2011)
- 3. Peak flux sometimes occurred during the day, and sometimes during the night, and DPR correctly and completely accounted for these time periods. Note, see pp8-14 and Tables 3 and 4, and figures 4-7
- 4. DPR concludes insufficient evidence exists to support most buffer zone credits, contrary to the U.S. E.P.A.'s conclusion. U.S. EPA credits were based upon a mix of field and lab column studies, while DPR uses only field studies in its analysis of credits. Although I am generally not in favor of credits for reducing buffer zones, this situation does pose a question of sound science, and whether EPA interprets 'sound science' differently than DPR. Model lab chambers, soil columns, and related techniques can provide good sound data particularly as related to variables such as wind speed and temp, which can be controlled in chambers but not in the environment. I would

encourage DPR to accept lab chamber and related data, if done according to sound science and GLP principles, but not necessarily for the result of providing credits for buffer distances. EPA and DPR are encouraged to exchange views on the use of data from model or lab champers, and when such data might be use, and under what circumstanes.

5. DPR utilized 1.25 m/s as the definition of a calm hour for wind speed and direction data from the California Irrigation Management Information System (CIMIS). Speeds at or below 1.25 m/s are considered calm hours for purposes of modeling and speeds above 1.25 are considered non-calm hours.

I do not have expertise in atmospheric meteorology sufficient to provide detailed comments on this poin, but I offer the following observations which may, or may not be to the point. DPR provided two references, both by Deaves and Lines to support the applicability of the Weibull distribution model to low wind speed data, ie over the complete windspeed range. This is possible because of the development of sonic or lightweight cup anemometers that respond at wind speeds below 1.25 m/sec, so that actual data is now available at those low wind speeds and it is not necessary to default to 1.25 m/sec when in fact actual wind speed values can be used at low wind speeds, including the CIMIS wind speed minimum reporting value of 0.447 m/s. DPR performed stochastic simulation which fit CIMIS recorded wind speed data to a Weibull distribution. This allowed DPR to better define a breakpoint at 1.25 m/s at which 20% of measurements are below the instrument threshold and 80% of measurements are above the threshold. (This reviewer recommends that this information and conclusion be added to the report that was provided for peer review, including a clear statement of why this better definition of the low wind speed reporting will improve establishment and enforcement of proposed buffer zones).

Unnumbered: The Big Picture

Some of this reviewer's comments, under the heading of 'general comments' are 'big picture' in nature.

DPR staff are commended for doing an exhaustive evaluation of possibilities for developing buffer zones. In particular, the detailed analysis of two state of the art flux models, PERFUM2 and FEMS, was well done. However, data from the Hydrus model is not included, but apparently will be in a future amendment to the report. This reviewer suggests that the present Report be indicated as open to updates periodically such as data from Hydrus, and perhaps the addition of new field study data. DPR might consider funding studies that shore up, or make more robust, the data in this report which was indicated to be of less than desireable volume, robustness, or quality. An example is for injection depth as an application variable that may affect flux. A few other examples, such as KTS barriers and soil moisture, are given as separate general comments.

Some results do not include an adequate statement or estimate of uncertainty. For example, Table 1, DPR Proposed buffer Zone Distances, p.10 (and Table 2, other tables specific to each application type), convey a degree of accuracy and precision that may not be supported by the data. DPR should consider adding a statement of uncertainty, eg +/- 5% to the proposed buffer zones to account for minor variations that might be allowable in practice when enforcing these proposed distances.

The report and proposed buffer zones do not appear to take into account the stability of chloropicrin in air as a plume drifts from a treated field down wind. Does DPR assume that cholopicrin in air is stable to reactions that might degrade the chemical, or to deposition process such as exchange with foliage or soil or water surfaces? Some statement should be added to the report addressing these potential mitigating effects, and if they are purposefully left out of the analysis and report, some recognition of these factors should be made, or simply to state that these factors are not considered in the proposed buffer zone distances.