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MEMORANDUM

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DATE: September 26, 2013

SUBJECT: COMMENTS ON THE DRAFT EXPOSURE ASSESSMENT DOCUMENT FOR PHOSPHINE

The Office of Environmental Health Hazard Assessment (OEHHA) has reviewed the draft Exposure Assessment Document (EAD) for occupational and ambient air exposure to phosphine (phosphorus trihydride), prepared by the Department of Pesticide Regulation (DPR), dated January 14, 2013. Our comments are provided in the attachment. We are currently reviewing the Risk Characterization Document (RCD) for Phosphine and will be sending comments on it separately. This review is conducted under the authority of Food and Agriculture Code Section 11454.1.

OEHHA has several general comments on the exposure assessment assumptions, methodology and conclusions of the draft EAD. These comments and our

recommendations, as well as some suggested clarifications, additions and corrections, are contained in the attachment.

Thank you for providing this draft document for our review. If you have any questions regarding OEHHA's comments, please contact Dr. Charles Salocks at (916) 323-2605 or me at (510) 622-3200.

Attachment

cc: Charles B. Salocks, Ph.D., D.A.B.T.
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Office of Environmental Health Hazard Assessment

OEHHA's Comments on DPR's Draft
Exposure Assessment Document for Phosphine

The Office of Environmental Health Hazard Assessment (OEHHA) is responding to a request from the Department of Pesticide Regulation (DPR) to comment on the draft Exposure Assessment Document (EAD) for phosphine [phosphorus trihydride]. OEHHA reviews risk assessments prepared by DPR under the authority of Food and Agricultural Code Section 11454.1, which requires OEHHA to conduct scientific peer reviews of risk assessments conducted by DPR.

BACKGROUND ON THE DOCUMENT

The draft EAD covers use of phosphine gas (in cylinders), and the phosphine-generating solids aluminum phosphide and magnesium phosphide, as fumigants used primarily indoors to control insect pests in raw agricultural commodities, animal feed and processed foods. It also covers outdoor uses to control rodents and moles. As pesticide products, aluminum and magnesium phosphide are formulated as tablets, pellets, granules and impregnated plates. They react with moisture in the atmosphere to produce phosphine gas. Cylinderized phosphine is formulated as pure phosphine gas for onsite dilution or as ready-to-use gas pre-mixed with 98% CO_2 to reduce explosion and fire hazard. These three compounds are restricted use pesticides that may be used only by specially trained and certified pesticide applicators. There is no homeowner or agricultural row crop uses for these products.

The exposure estimates generated in this document were organized according to the type of fumigation or aeration performed (commodity, space, spot, or burrowing rodent fumigation), the type of structure fumigated, and the exposed populations. The EAD provided estimates of phosphine exposure for workers and bystanders exposed to phosphine gas during and after fumigation activities. Structures where these fumigants are applied include concrete upright bins of grain elevators, farm bins, flat storage facilities, warehouses, rail cars, box cars and ships. The exposed populations were fumigant applicators (present within or located outside the fumigated structure), workers who aerate structures, workers who assist in application and aeration, workers who retrieve the spent fumigant, various types of occupational bystanders, and residential bystanders. No exposure data were available on exposures resulting from use of cylinderized gas and granular formulations by applicators, aerators and bystanders, so DPR adopted default assumptions to generate surrogate exposure estimates.

OEHHA's comments are provided below. A summary of the major comments is first presented, followed by general comments and more detailed specific comments.

SUMMARY OF COMMENTS

The document is focused on phosphine as a fumigant and a related exposure assessment, but unfortunately limited data are available and the many gaps require assumptions to complete the assessment. Overall, the document addressed the important issues. The writing and especially the organization of the document could benefit from additional internal review and editing. Our principal comments and suggestions are as follows:

- It would be helpful if the scope of the EAD were clarified in the title, abstract and introduction by indicating that it covers exposures from the use of specific pesticides. However, exposure to the rodenticide zinc phosphide (for which there are several products registered for use in California) was not included in the assessment, and an explanation why that was the case could be provided.

- A screening evaluation of potential percutaneous absorption as an exposure pathway could be added to provide screening level estimates of absorbed doses – both from phosphine vapor and phosphide dust. This is needed to assess the significance of this dermal pathway relative to the inhalation pathway.

- Precautions regarding the appropriate use of respiratory protection need to be clarified. Specifically, it is unclear whether standard practices and precautions against entering an environment where the phosphine concentration is unknown or when monitoring equipment is unavailable are sufficient to prevent significant exposures. Further consideration of these scenarios is warranted in the EAD.

- The assumption, stated on pages 37, that occupational bystanders, working both inside and outside of grain elevators during fumigant application and commodity fumigation, will wear full-face respirators is not likely to hold. Consequently, the short-term exposure estimates presented for occupational bystanders in Table 13 do not represent "baseline" exposure estimates, but would be expected to be higher.

- Given the extreme acute toxicity of phosphine, OEHHA recommends that DPR conduct more in-depth evaluation of several short-term exposure scenarios. For example, in studies of aluminum phosphide applicators, the airborne concentrations detected would be well in excess of disabling or life-threatening

levels unless full-face respirators were worn. These results indicated that short-term exposures to phosphine were episodic and brief (less than 5 minutes), and occurred several times each day. In contrast, data from occupational studies where samples were collected over several hours do not reflect these very short concentration excursions. OEHHA recommends that DPR review the "instantaneous" exposure data and the analysis of short-term exposure to ensure that averaging of short-term peak concentrations over long-term sampling durations does not mask the potential for acute health effects.

- An exposure scenario that is not addressed in the EAD is the potential for phosphine to continue to "off-gas" (that is, be re-released) from fumigated materials after a facility or storage structure has been aerated. OEHHA recommends that DPR consider examining such a scenario, and attempt to estimate post-aeration exposure concentrations that might be produced in confined spaces.

- DPR appears to have not considered data from two different sources (the Pesticide Use Report database and the 2002 phosphine worker exposure study conducted by Dagesch America) that would lead to higher exposure estimates. These data may be useful in the exposure calculations for the various scenarios. If not, it would be helpful if the rationale for not including these data is revisited or additional justification be provided.

- A number of editorial comments and suggestions are also provided for your consideration.

GENERAL COMMENTS

Scope of the EAD

One pesticidal source of phosphine exposure that was not evaluated in the EAD is pesticidal use of zinc phosphide (used in rodenticide baits). An explanation in the introduction why zinc phosphide, a rodenticide, was excluded from the EAD would be helpful. Also, since the EAD looks at exposure resulting from the pesticidal use of phosphine, aluminum phosphide and magnesium phosphide, it would be more precise and informative for the document to be titled "Estimation of Exposure to Persons in California to Phosphine from Pesticidal Use of Phosphine, and Magnesium and Aluminum Phosphide".

Industrial use of phosphine in semiconductor manufacturing and chemical syntheses, and natural occurrence resulting from anaerobic decomposition of organic matter or

sewage treatment plant sediments, represent additional potential sources of phosphine exposure. A brief mention of this might be informative for many readers of the document.

Dermal Absorption of Phosphine Vapor and Phosphide Dust

Potential dermal absorption of phosphine was noted and discussed briefly on pages 11-12. The discussion included the following statement, excerpted from the U.S. Environmental Protection Agency's (U.S. EPA) 1998 Reregistration Eligibility Decision document for aluminum and magnesium phosphide: "Because the route of exposure anticipated for aluminum and magnesium phosphide is inhalation, the Agency does not expect significant dermal exposure. Therefore, dermal absorption studies are not required." Similarly, the document quotes from Hayes (1982), "The effectiveness of proper gas masks excludes the possibility of significant absorption by the skin." Both of these statements should be justified more explicitly.

In a quantitative health risk assessment, an exposure pathway may be excluded if it is shown using screening-level assumptions that it is not significant in comparison to other complete exposure pathways. Neither U.S. EPA nor DPR presented an analysis using screening-level assumptions to show that dermal exposure is not significant in comparison to other complete exposure pathways. In a recent review, Rehal and Maibach (2011) cited several proposed methods for mathematically modeling percutaneous absorption of chemical vapors (e.g.,Kezic et al. 2000) that DPR could utilize. Additionally, DPR could calculate an upper bound estimate of dermal exposure using measured air concentrations and a calculated skin permeation coefficient (Klein 2000). Such an assessment could be used to estimate the significance of percutaneous absorption relative to inhalation and provide justification for determining whether dermal exposure to phosphine is an issue that warrants more detailed, in-depth evaluation in a human health risk assessment.

The dermal absorption pathway may be of particular concern in scenarios where the airborne concentration of phosphine is high and a high level of respiratory protection (e.g., a full-face respirator or a self-contained breathing apparatus (SCBA)) is required. Under these conditions, the significance of dermal absorption of vapor relative to inhalation uptake is likely much greater because the latter is substantially mitigated by the use of personal protective equipment.

Dermal absorption of phosphide dust is another potential exposure pathway that warrants additional consideration in the EAD. On page 89, DPR described a study by Baker (1992), who observed that relatively high levels of phosphine were given off by

the clothing of workers who had handled aluminum phosphide tablets, and whose clothing became contaminated with dust from the tablets. In the *Medical Management Guidelines for Phosphine*, the Agency for Toxic Substances and Disease Registry (ATSDR) stated, "Most phosphine exposure occurs by inhalation of the gas or ingestion of metallic phosphides, but dermal exposure to phosphides can also cause systemic effects".

Regarding dermal absorption of phosphine vapor and metal phosphide dust, the Exposure Appraisal section (page 97) concluded that "...due to lack of data, percutaneous absorption was not factored into the exposure estimates. This may have *led to an underestimation of exposure." To evaluate the magnitude of underestimation,* OEHHA suggests that DPR evaluate the dermal exposure pathway in greater detail to determine whether screening level estimates of absorbed doses – both from phosphine vapor and phosphide dust – can be derived, and if so, provide such estimates.

Personal Protective Equipment (PPE) and Respiratory Protection

The first paragraph of this section, which begins on page 17, includes a statement that a self-contained breathing apparatus (SCBA) must be used when the air concentration of phosphine is unknown or exceeds 15 ppm. It also states that certain product labels indicate that a SCBA must be worn if the phosphine concentration is unknown or exceeds the short-term exposure limit of 1 ppm for 15 minutes. Still other labels indicate that an approved canister respirator must be worn if monitoring equipment is not available. Since phosphine concentration is unknown when monitoring equipment is not available, these recommendations appear to contradict one another: they indicate in one case that SCBA must be used when the concentration is unknown and in another that an approved canister respirator is appropriate for these situations. A statement pointing out this discrepancy should be included in the EAD. If the concentration is truly unknown, there is no basis for selecting the appropriate level of respiratory protection. Ultimately the effectiveness of different label requirements for mitigating exposure to phosphine may need to be evaluated more carefully in the EAD.

Similarly, the second paragraph on page 18 begins with the statement, "For indoor applications, all of the product labels contain the requirement that an approved full-face gas mask-phosphine canister combination or SCBA or its 'equivalent' to be available *within the structure being fumigated"* [italics added]. The next sentence states, "The Detia® FUMEX product label contains the statement, 'If SCBA or its equivalent is not available at the application site, it must be available locally, for example, *at a fire station or rescue squad*'" [italics added]. These two statements seem to contradict one another. While neither scenario guarantees that an SCBA unit will be used when

necessary, the presence of an SCBA unit at a local fire station – which could be miles from the fumigated structure – provides considerably less assurance that the unit will actually be used than if it were located within structure being fumigated. Later in this section, the discussion of precautions to be taken when using cylinderized phosphine gas indicates that respiratory protection must be available *at the site of application*. Overall, one would expect the respiratory protection requirements for use of aluminum and magnesium phosphide to be consistent with those stipulated for phosphine gas. If the labels for these products are inconsistent with one another with respect to the availability of SCBA (as they appear to be), then these inconsistencies should be addressed directly in the EAD. Ultimately the effectiveness of different label requirements for mitigating exposure to phosphine may need to be evaluated more carefully in the EAD.

On page 37, occupational bystanders working both inside and outside of grain elevators during fumigant application and commodity fumigation were assumed to wear full-face respirators. This scenario assumes (1) that the airborne concentration of phosphine is known to all workers in the vicinity of the fumigation, even those not directly engaged in fumigation activities, (2) that full-face air-purifying respirators (APRs) are available for all workers and all bystanders, and (3) that the APRs have been fitted with the appropriate air filtration cartridges. OEHHA is concerned that these assumptions may be overly optimistic in many circumstances, and would be interested in seeing the results of any occupational surveys on this subject, if available. Consequently, the short-term exposure estimates using these scenarios presented for occupational bystanders in Table 13 may not reflect "baseline" exposure estimates, but rather provide values that assume that an exposure mitigation strategy is in place at all locations where these fumigants are used and is effective 100 percent of the time. Therefore the estimated exposures are expected to be higher. We are concerned that bystanders might lack adequate respiratory protection, consistent with what has also been expressed by U.S. EPA: "...the Agency is concerned about the potential risks posed to occupational and residential bystanders who are not likely to be wearing the necessary respiratory protection" (U.S. EPA 1998).

The discussion of respirator selection on pages 17 and18 could be improved by including the protection factor provided by the different types of respirators (e.g., 99% protection afforded by a full-face air-purifying respirator).

Other Exposure Scenarios

An exposure scenario that is not addressed in the EAD is the potential for phosphine to continue to "off-gas" (that is, be re-released) from fumigated materials after a facility or storage structure has been aerated. From the results of the studies described on pages

11 and 12 ("Dermal Absorption of Phosphine"), it is clear that phosphine is capable of penetrating deep into porous building materials such as concrete and cinder block as well as biological materials such as baled sheep skins and wheat grain. DPR recently completed a series of intensive investigations demonstrating that high levels of methyl bromide can accumulate in enclosed spaces after aeration of fumigated grapes at the Port of Los Angeles, and it would be reasonable to conclude that off-gassing of phosphine-fumigated commodities also might have the potential to lead to a high-risk exposure scenario. OEHHA recommends that DPR consider examining such a scenario, and attempt to estimate post-aeration exposure concentrations that might be produced in confined spaces.

Excluding Some Pesticide Use and Monitoring Data

The paragraph at the bottom of page 16 states that 27 percent of the use data for aluminum phosphide on dry flowable commodities (grains and nuts) were assumed to be erroneous because they exceeded the product label maximum application rate. (These data were abstracted from DPR's Pesticide Use Report (PUR) database for the five-year period from 2006 through 2010.) Additional justification for excluding these data from calculation of seasonal application rates needs to be provided. An alternative assumption is that use of aluminum phosphide at levels above those specified on the product label is not an uncommon occurrence.

The first paragraph on page 27 begins, "No background PH_3 [phosphine] air concentration data were available for the TWA [time-weighted average] samples in either the registrant or NIOSH [National Institute for Occupational Safety and Health] studies. The registrants generated background samples via opening the sampling tube and then immediately sealing the tube for analysis. These samples were not used however, since they generated a false-positive signal that increased with increasing storage time...This instability was not present in their field fortification samples." It is unclear why DPR concluded that the phosphine concentrations detected in these samples represented false positive results, particularly if they were replicated in multiple samples. In light of the possibility, noted above, that building materials and stored grain have the capacity to absorb and re-release phosphine, an alternative hypothesis is that the background samples actually captured low levels of phosphine that were present in the ambient environment under investigation. Depending on where and how the background samples were stored, it is conceivable that the phosphine concentration in the sample tubes might increase, perhaps because they were stored in close proximity to materials that had previously absorbed the pesticide. Low background levels of phosphine would not necessarily be detected in field fortification samples if the latter had been spiked with a substantially higher concentration of phosphine. OEHHA

recommends that DPR consider alternative explanations for the results that were obtained in these studies. If exposure to low background levels of phosphine occurs in certain exposure scenarios, then background exposure needs to be accounted for in the EAD.

SPECIFIC COMMENTS

Pharmacokinetics

The dermal absorption data cited in this section of the document are of very poor quality. DPR determined that they could not identify an acceptable quantitative study and concluded that these results should not be used in the EAD. OEHHA agrees with this determination. A statement that the available pharmacokinetic data are not of sufficient quality for human health risk assessment, and a discussion of the deficiencies of the available studies that justifies this conclusion, should be included in the EAD.

OEHHA agrees with the use of a health-protective default value of 100 percent for inhalation absorption rate since no experimental data are available.

Information on phosphine metabolism is limited. Although the report recognized the data gap, their description of the Lyubimov and Garry review is too succinct and would benefit from inclusion of additional detail (Lyubimov and Garry 2010).

Reported Illnesses

The EAD covers phosphine- and metal-phosphide related illnesses for the five-year period spanning 2005 through 2009, based on information obtained from the California Pesticide Illness Surveillance Program (PISP) database. During this period, 10 cases of phosphine exposure were reported to have resulted from use of aluminum phosphide. However, 15 additional cases of phosphine exposure from aluminum phosphide use were reported in 2010. Similarly, in addition to the 27 cases of phosphine exposure resulting from use of cylinderized phosphine reported from 2005 through 2009, 14 cases were reported in 2004. To provide a more comprehensive description of actual scenarios for inadvertent or accidental exposure to phosphine, OEHHA recommends that this discussion include phosphine exposure cases reported during the period from 2004 through 2010.

Pesticide Use and Sales

Even though DPR used the latest available pesticide use report (PUR) data (2006-2010), the EAD should clearly indicate that PUR data only cover use in agricultural settings, and that use of zinc phosphide is not included. If the overall volume of

phosphine and phosphine-generating compounds sold in California is available, it would be possible to compare the amount sold for pesticidal use to the total amount sold in order to evaluate the importance of non-agricultural use.

Updates to Product Labels

OEHHA suggests that EAD include a sample label for each type of pesticide product in the appendix or a link to their location on DPR's website. The following two updates related to label information should be provided as well:

- Since 2010, new restrictions apply to all phosphine products for use against burrowing rodents (http://www.epa.gov/oppsrrd1/reregistration/alphosphide/aluminum-magnsm-phos-fs.html).
- An amendment to increase the application rate for cylinderized phosphine to match metallic phosphide labels was submitted to U.S. EPA on February 4, 2013, and accepted on March 12, 2013 (EPA Registration No. 68387-8).

Environmental Concentrations and Environmental Fate

The EAD did not include a section on environmental concentrations or environmental fate. Consequently, these processes cannot be incorporated into bystander and residential exposure scenarios. This information is available in other reports for phosphine (DPR 2013, EFSA 2012, U.S. EPA 1998) and in other EADs that OEHHA recently reviewed. If no data are available or if phosphine is not found in the ambient environment, then a statement to this effect should be included in the EAD.

Exposure Assessment

A registrant task force study (Degesch America 2002) was available for workers fumigating/aerating farm bins and flat storage facilities, warehouses, rail cars and equipment, and specific areas of a flour and corn mill (spot fumigation). NIOSH studies (NIOSH 1986a, b; 1987a, b) were also available for occupational exposure following commodity fumigation in concrete upright bins of grain elevators. Results from the NIOSH studies were combined with the registrant study in the exposure assessment. No data were available to document applicator, aerator and bystander exposures following use of cylinderized gas and granular formulations, so exposures were estimated using data from other facilities as surrogates. Although this appears to be reasonable, the decision to utilize surrogate exposure estimates would benefit from additional discussion and justification, and the consequent uncertainties should be articulated.

A California Air Resources Board (CARB) study (CARB 2008) of occupational and residential bystanders following commodity fumigation of concrete upright bins of grain elevators and farm bins was available, but DPR decided not to use these results for the bystander risk assessment because of poor data quality (bad recoveries and sample loss). OEHHA concurs with DPR's determination that inclusion of the CARB study might lead to underestimation of exposure.

In cases where data were lacking and no surrogate exposure estimates could be applied, exposures were based on the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL). A PEL is the maximum permitted 8-hour time-weighted average (TWA) concentration of an airborne contaminant during a 40-hour work-week. The PEL for phosphine is 0.3 parts per million (ppm). When the air concentration exceeds the PEL, workers (applicators as well as occupational bystanders) are required to use full-face respirators. The short-term exposure limit (STEL, a 15-minute TWA exposure that is not to be exceeded at any time even if the 8 hour TWA is below the PEL) is 1 ppm. Given the variability of actual exposure conditions that may exist when various facilities are fumigated (e.g., situations where the air concentration of phosphine is unknown or monitoring equipment is not available, as discussed on page 18 of the EAD), the validity of assuming that exposure concentrations will not exceed the PEL or the STEL is questionable, even if these values are legally enforceable. OEHHA recommends that DPR discuss the uncertainties associated with this assumption and provide additional justification for adopting it.

To estimate seasonal exposure, DPR used the arithmetic mean of the measured air concentrations, after correcting for recovery (if <90%), and then multiplying by the ratio of the estimated seasonal application rate to the application rate used in the exposure study. According to an internal DPR memorandum (2003), the arithmetic mean better reflects the expected magnitude of exposure compared to the median or geometric mean. OEHHA agrees that the arithmetic mean is a better estimate for this purpose than the median or geometric mean. OEHHA recommends taking the 90% or 95% upper confidence limit (UCL) of the arithmetic mean to estimate intermediate and long term exposures when the monitoring data are sufficiently robust to support a high-end estimate of the mean. In addition, it may not be valid to multiply the measured air concentration by the ratio of the label maximum application rate to the application rate used in the exposure study when the rates are very different. This approach assumes that the measured air concentration varies linearly with the application rate, and the EAD needs to provide justification for this assumption.

Short-term Exposure Spikes

As noted above, the STEL for phosphine is 1 ppm. Phosphine has a sharp acute dose-response relationship, ranging from little apparent effect to death just by doubling the dose (from 5 to 10 ppm in animal studies). Symptoms typically appear within the first few hours and continue to develop for days or weeks after exposure has ceased. The NIOSH studies included evaluation of short-term exposure to phosphine from the handling of aluminum phosphide tablets or pellets, as described on page 25 of the EAD. In these studies, breathing zone samples with a sampling period duration of five minutes or less (referred to as "instantaneous" in the EAD) were collected from applicators while they were filling and emptying fumigant auto-dispensers or manually adding fumigant to grain. Filling or emptying auto-dispensers was assumed to take about five minutes and to occur up to seven times each day. Airborne phosphine concentrations ranged from 0.1 to 52 ppm; the average concentration was 11.3 ppm. OEHHA recommends that the number of samples collected in these studies be indicated in the EAD.

The data from the NIOSH studies of aluminum phosphide applicators indicate that short-term exposures occur relatively frequently during the work day, and that the airborne concentrations that are present during commodity fumigation are high. OEHHA agrees that if full-face respirators (which are assumed to provide a 99% protection factor) are used, short term exposure to the concentrations detected in the NIOSH studies should not be a concern. However, given the short-term nature of exposure and the number of exposure events that occur each day, it appears that there is at least some potential for applicators not to wear full-face respirators each and every time when needed. Furthermore, short-term use of full-face respirators by occupational and residential bystanders should be regarded as less likely to occur. Since the use of full-face respirators is a critical aspect of the exposure assessment, the uncertainties inherent in assuming that they are always used appropriately in these settings need to be discussed in the EAD.

In the description of the short-term samples obtained by NIOSH, DPR stated, "Due to the extremely short exposure periods (i.e., ~5 minutes), the instantaneous samples were not directly used to estimate work shift exposures. However, these episodic exposures would *have been incorporated into the TWA samples* [italics added] which were also collected from the workers and were used for estimating exposure" (page 25). However, OEHHA questions whether 3- and 6.8-hour TWA sample data (the durations of samples collected in the registrant and NIOSH studies, respectively) are appropriate to assess the potential short-term health risk of phosphine. Assuming that short-term exposure peaks occur infrequently, averaging them over an 8- or 24-hour day essentially eliminates them. For example, assuming that a worker was exposed to 4

ppm for 15 minutes during an 8-hour work day, the TWA exposure concentration would be just 0.125 ppm, well below the PEL. Nevertheless, the likelihood that this individual's health would be adversely affected would be high. OEHHA recommends that DPR review the "instantaneous" exposure data and the analysis of short-term exposure to ensure that averaging of short-term peak concentrations does not mask the potential for acute health effects.

Exposure Appraisal

The General Assumptions section (page 97) said, "The first assumption is that the handler and occupational bystander are located in the highest use county for the entire season. This assumption, however, may be incorrect, leading to overestimation of exposure." OEHHA does not believe this is an assumption that leads to overestimation but rather that it represents a "plausible worst case" scenario. Since exposure assessments should be conducted using reasonable worst-case assumptions that are consistent with product labels, this assumption does not appear unrealistic.

EDITORIAL COMMENTS

The following elements are suggested for enhancing the document: numbering of the chapters and section; inclusion of examples of product labels; inclusion of data from the original studies when the results of different studies are combined in tables; and inclusion of a description and summary of the individual exposure studies once in their entirety early in the document which can then be referenced later in the document as appropriate.

The first paragraph of the Abstract (page 4) states, "The peak phosphine exposure estimates presented below consist of short-term and seasonal exposure estimates." The use of the term "peak" in this sentence and elsewhere is not clear. Is the report referring to the maximum concentration observed within recording time (that is, a concentration spike) or the highest concentration observed within the different sampling periods used in the registrant and NIOSH studies (that is, the highest concentration observed over a 3- or 6.8-hour interval)?

The second paragraph of the Abstract summarizes short-term (< 24-hour) exposure estimates for commodity fumigation of eight different types of structures. This information would be best presented as a table. Text could then be used to highlight important findings of the analysis.

Although very concise, the Abstract would be more informative by providing a rationale for selection of the different time-weighted average exposure calculations (8-, 9.7-, 12-

and 24-hours). Additionally, it could identify and briefly discuss the field studies that provided a basis for the estimated air concentrations.

The title for Figure 1 (page 13) needs to indicate that these pesticide use data are for California only.

The phosphine use data detailed in the text on pages 15-17 would be more easily understood if it were summarized in tables, which could highlight parameter values that are critical to the exposure assessment. Additionally, the fact that different units were used to characterize the amount, area or volume of use in the PUR database (pages 16-17) is a detail that does not appear to merit discussion in the main body of the report.

The first paragraph at the top of page 18 refers to Table 8. The referenced information is provided in Table 7.

The section on physical and chemical hazards of phosphine (page 19) refers to the "lower flammability limit" of 1.8% v/v. The correct term is lower *explosive* limit (LEL).

Statements that measured air concentrations from field studies were corrected for recovery if the recovery was <90% appear numerous times throughout the EAD, both in the text and in the tables. While a limited degree of redundancy is desirable in a detailed technical report, the fact that a description of the recovery correction procedure appears dozens of times in the EAD is excessive. OEHHA recommends that DPR provide a detailed description of the recovery correction procedure and an example calculation at the beginning of the report, and then refer to the page or section where this description is provided when necessary. For example, "If recovery from field fortification studies was less than 90%, data were corrected using the procedure described on page xx."

OEHHA suggests that DPR consider adding an introductory section that provides a general overview of the exposure scenarios at the beginning of the Exposure Assessment section (page 22), as was done in other EADs (e.g., chloropicrin and simazine).

The last paragraph on page 24 includes a detailed technical description of NIOSH method S322 for analysis of airborne phosphine concentrations in field samples. This level of detail is not needed in the body of the exposure assessment document and probably could be moved to an appendix.

Quantitative information and data that are presented as text in the EAD can often be summarized in tables that are much easier for the reader to comprehend. For example, most of the text in the second paragraph on page 26, which describes the results of the NIOSH grain elevator studies, can be summarized as follows:

Type of Application	n	Sampling Time (min)	Application Rate (g/bushel)	Mean Air Concentration (ppm)	Highest Air Concentration (ppm)
Auto-dispenser	26	335	0.05	0.52	1.67
Manual	9	219	0.04	0.05 (adjusted)	0.13 (adjusted)

In the Exposure Assessment section, OEHHA suggests that DPR provide an example of each major calculation and a description of how the information presented in the tables was used to provide details and exceptions for each individual exposure scenario. The text provided excessive details regarding the content of the tables (e.g., entire paragraphs regarding the number of replicates) and the same studies were described multiple times for each applicable scenario. It would be more efficient to describe fully each major study once and use tables to highlight the concentration data that are relevant to each scenario.

The first line of page 23 ends with "(HSM-03002)." It is not clear that this is actually a reference, and that the reference is a 2003 internal DPR memorandum from Sally Powell to Joe Frank. For clarity, OEHHA suggests that this memo be cited as "(Powell 2003)." (Note too that the correct memo designation is HSM-03022.) Similarly, "HSM-09004" could be cited in the text and references section by the author and year of preparation.

On page 25, the second paragraph includes the statement, "The phosphine air concentrations, in the absence of respiratory protection, ranged from 0.1 to 52 ppm with a mean value of 11.3 ppm." Note that it is the exposure, not the air concentration, is reduced by the use of PPE. Similarly, the first sentence on page 35 reads: "The occupational bystander scenario with the highest exposure value was used to estimate occupational bystander exposure post-aeration of the fumigated commodity." Does this refer to the highest exposure value or the highest airborne concentration?

On page 53, it would be more informative to state that the annual exposure estimate for the commodity fumigation/flat storage facility applicator was based in part on the assumption that fumigation occurs 8 months out of the year.

In the section titled "Bulk Car Fumigation and Aeration" (page 62), two sub-sections address the exposure of occupational bystanders (pages 64 and 67). It would be helpful if DPR specified the type of occupational bystanders in the title of the sub-section (during application or during aeration) to help distinguish them.

On page 67, the two-sub-sections "Assistant Operator" and "Occupational Bystander" were not included in the Table of Contents (page 2). There also appears to be a formatting difference: these titles, unlike the other ones in the same section, are underlined.

On page 76, change "Tables 19" to "Table 19."

Under the heading "Ship Hold" (page 77), the second sentence reads: "These [five] studies are presented in journal articles containing air monitoring data for a total of five ships carrying grain (e.g., corn and wheat)." References (author, year published) for these studies should be provided parenthetically immediately at the end of this sentence. Also, the first study was included in the registration package from Phos-Fume Chemicals Company, Ltd., and does not appear to have been published. Therefore it is not a journal article. Later in this section (page 80) a line needs to be inserted between the second and third lines to separate the discussion of the fourth and fifth studies.

On page 96, the entire second paragraph in the "Occupational Bystander" section referred to residential bystanders. This should be re-located to the residential bystander section.

References

Agency for Toxic Substances and Disease Registry Medical Management Guidelines for Phosphine. http://www.atsdr.cdc.gov/mmg/mmg.asp?id=1013&tid=214.

Baker, R.O., Exposure of Persons to Phosphine Gas from Aluminum Phosphide Application to Rodent Burrows. Proc. 15th Vertebrate Pest Conf. (J.E. Borreco and R.E. March, Editors) Published at University of Calif., Davis, 1992.

CARB (2008) Report on Air Monitoring of the Application of Phosphine in Merced County in December 2008. Air Resources Board, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/emon/pubs/tac/phosphine.htm.

Degesch America (2002) Registration Package 51882-015. Phosphine Worker Exposure. Registration Resource Center, Division of Registration and Health Evaluation, Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St, P.O. Box 4015, Sacramento, CA 95812-4015.

DPR (2003) Why Worker Health and Safety Uses Arithmetic Means in Exposure Assessment. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/whs/memo/hsm03022.pdf. HSM-03022.

DPR (2013) Phosphine Risk Characteriation Document. Medical Toxicology Branch, Department of Pesticide Regulation, California Environmental Protection Agency.

EFSA (2012) Conclusion on the peer review of the pesticide risk assessment of the active substance phosphane. European Food Safety Authority. EFSA Journal 2012;10(3):2595

Hayes, W.J.J. (1982) Pesticides Studied in Man, Williams and Wilkins Publishing Co., Baltimore, Maryland.

Kezic, S., Monster, A.C., Kruse, J. and Verberk, M.M. (2000) Skin absorption of some vaporous solvents in volunteers. Int Arch Occup Environ Health 73(6), 415-422.

Klein, C., Mathematical Models for Estimating Occupational Exposure to Chemicals paper presented at the American Industrial Hygiene Association (AIHA), Exposure Assessment Committee, 2000.

Lyubimov, A.V. and Garry, V.F. (2010) Handbook of Pesticide Toxicology, pp. 2259-2266, In Krieger R., Hayes Amsterdam: Elsevier, Inc.

NIOSH (1986a) In-Depth Industrial Hygiene Survey Report of the Bunge Corporation, Kansas City, Kansas (Report Number 149.10). Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies National

Institute for Occupational Safety and Health, Centers for Disease Control, Cincinnati, Ohio. 149.10.

NIOSH (1986b) In-Depth Survey Report of Early and Daniel Co., Inc., Louisville, Kentucky (Report Number 149.12). Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies National Institute for Occupational Safety and Health, Centers for Disease Control, Cincinnati, Ohio. 149.12.

NIOSH (1987a) Composite Report: Industrial Hygiene Characterization of Grain Elevator Workers' Exposures to Phosphine during Bulk Grain Fumigation with Aluminum Phosphide. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health. Composite Report.

NIOSH (1987b) In-Depth Survey Report of Scoular Elevator, Salina, Kansas (Report Number 149.18). Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies National Institute for Occupational Safety and Health, Centers for Disease Control, Cincinnati, Ohio. 149.18.

Rehal, B. and Maibach, H. (2011) Percutaneous absorption of vapors in human skin. Cutan Ocul Toxicol 30(2), 87-91.

U.S. EPA (1998) Reregistration Eligibility Decision (RED) AL & Mg Phosphide. Office of Pesticide Programs, United States Environmental Protection Agency, Washington, D.C. http://www.epa.gov/oppsrrd1/reregistration/REDs/0025red.pdf.