

Texas Commission on Environmental Quality Response to Public Comments

Propionaldehyde Development Support Document (DSD)

Dr. Thomas Dydek, on behalf of Eastman Chemical Company, submitted comments dated February 16, 2015, on the October 27, 2014, Development Support Document for Propionaldehyde. The Texas Commission on Environmental Quality (TCEQ) appreciates the effort put forth in providing comments on the proposed DSD for propionaldehyde. The comments made on behalf of Eastman Chemical Company are provided below, followed by TCEQ responses.

Comment No. 1, Odor ESL for Propionaldehyde:

The commenter states that setting the odor effects screening level (ESL) at the geometric mean of the commenter's suggested odor threshold values (1 ppb, 9 ppb, and 640 ppb) would be more in keeping with agency policy.

The TCEQ finalized a new guidance document, "Approaches to Derive Odor-Based Values," in September 2015. As described in this guidance document, if available data indicates the chemical of interest actually has a pleasing odor at low concentrations but an offensive odor at higher concentrations, a higher odor threshold value may be used for the odor-based ESL. Propionaldehyde has broad range of odor threshold values. It has a strong odor at high concentrations but has a pleasing scent at very low concentrations. As a result of the new odor guidance document, a revised odor ESL was established for propionaldehyde at a higher odor threshold value, i.e., a 50% odor recognition threshold value of 40 ppb ($92 \mu\text{g}/\text{m}^3$). The revised odor-ESL is higher than the geometric mean of the commenter's suggested odor threshold values (1, 9, and 640 ppb).

Comment No. 2, Long-Term Effects Screening Level (ESL) for Propionaldehyde:

The commenter suggested using the Gage (1970) study as the key study for derivation of the long-term ESL, to result in a long-term ESL of $67 \mu\text{g}/\text{m}^3$.

The Propionaldehyde DSD will not be revised based on this comment. The lack of study details, unknown study quality, and use of nominal concentrations and not analytical concentrations were decisive reasons why the Gage (1970) study was not chosen as the key study. The Union Carbide (1970) study was used by the TCEQ as the key study in derivation of the long-term ESL for propionaldehyde, with the Gage (1970) study serving as a supporting study.

COMMENTS ON THE PROPOSED TCEQ EFFECTS SCREENING LEVELS FOR PROPIONALDEHYDE

I. INTRODUCTION

This report contains the results of my review of the proposed Texas Commission on Environmental Quality (TCEQ) Effects Screening Levels (ESLs) for propionaldehyde. The current published short- and long-term ESLs for propionaldehyde are 20 $\mu\text{g}/\text{m}^3$ and 46 $\mu\text{g}/\text{m}^3$ respectively (TCEQ, 2014a). The short-term ESL is based on the odor threshold for this chemical and the long-term ESL is based on health effects. The proposed new ESLs of 22 $\mu\text{g}/\text{m}^3$ and 40 $\mu\text{g}/\text{m}^3$ respectively are found in the recently published Development Support Document (DSD) for propionaldehyde (TCEQ, 2014b). The current report contains my comments on the ESLs proposed in the DSD.

II. BACKGROUND INFORMATION ABOUT PROPIONALDEHYDE

Propionaldehyde is a water-white liquid at ambient temperatures and pressures. It has a molecular weight of 58.08 and a vapor density of approximately 1.8. The vapor pressure of propionaldehyde is 317 millimeters of mercury at 25 degrees Centigrade. The odor of this chemical has been described as fruity and acetaldehyde-like (HSDB, 2015).

Industrial uses of propionaldehyde include the manufacture of propionic acid and polyvinyl and other plastics. It is also used in organic chemical synthesis and as a disinfectant and preservative (Lewis, 1993). Propionaldehyde is a skin, eye, and respiratory tract irritant (ACGIH, 2002; HSDB, 2015).

III. COMMENTS ON PROPOSED SHORT-TERM ESL FOR PROPIONALDEHYDE

The short-term ESL proposed in the recent DSD for propionaldehyde is 22 $\mu\text{g}/\text{m}^3$, based on odor threshold data. The DSD lists six different sources for odor threshold data for this chemical. Of these, only two are from peer-reviewed journal articles using well-described methodologies (Nagata, 2003 and Hellman and Small, 1974). The odor threshold values from those two studies are 1 part per billion (ppb) and 9 ppb respectively. These values are equivalent to 2.4 and 21 $\mu\text{g}/\text{m}^3$.

The DSD also quotes the results of a computation of the "level of distinct odor awareness" (LOA) for propionaldehyde. The LOA for a particular chemical is an airborne level of that chemical above which more than half of the population will experience a "distinct odor intensity". These values are computed as part of the setting of Acute Exposure Guideline Levels (AEGs) by the National Academy of Sciences Committee on Toxicology. The LOA for propionaldehyde (based on the laboratory-derived odor threshold data) is 640 ppb, or 1,521 $\mu\text{g}/\text{m}^3$ (NAS, 2009).

Citing uncertainty in the laboratory-derived odor thresholds and the fact that the LOA value for propionaldehyde is much greater than those values, the TCEQ concluded in the DSD that the current odor-based ESL of 9 ppb or 22 $\mu\text{g}/\text{m}^3$ (from the work of Hellman and Small) should be used as the short-term ESL for propionaldehyde. This seems like an arbitrary choice.

It is agency policy (TCEQ, 2012) that when multiple acceptable sources of odor threshold data are available, the geometric means of different values should be used to determine an odor-based ESL. If one is to put weight on each of the odor threshold values above (the 1 ppb of Nagata; the 9 ppb of Hellman and Small; and the 640 ppb of NAS), setting the ESL at the geometric mean of those three values would be more in keeping with agency policy.

The geometric mean of these three values is 17.9 ppb, or 48 $\mu\text{g}/\text{m}^3$. There is a degree of conservatism in this approach since the LOA for propionaldehyde was based on a laboratory-derived odor threshold of 1.6 ppb (NAS, 2009). Furthermore, in a human exposure study in which volunteers were exposed to 134 ppm (317,000 $\mu\text{g}/\text{m}^3$) of propionaldehyde for 30 minutes, there was only an "occasional comment about the odor of the substance" (Sim and Pattle, 1957). This human data suggests that the actual level at which humans detect the odor of propionaldehyde may be quite a bit higher than the 48 $\mu\text{g}/\text{m}^3$ calculated above.

The short-term health-effects-based ESL proposed in the DSD for propionaldehyde is 500 $\mu\text{g}/\text{m}^3$. Since this is considerably higher than the odor-based short-term ESL, no comments on the accuracy of the health-effects-based ESL is needed.

IV. COMMENTS ON PROPOSED LONG-TERM ESL FOR PROPIONALDEHYDE

The toxicity database for propionaldehyde is not at all extensive, especially for human data. The key study identified in the DSD on which to base a long-term ESL for propionaldehyde was an unpublished report from the Union Carbide Company (Union Carbide, 1993). In this study, rats were exposed to 0, 150, 750, and 1,500 ppm of propionaldehyde six hours per day for 52 days (males) or 48 days (females).

Effects were seen even at the lowest exposure level, thus no NOAEL could be determined. The 150 ppm level was identified as the LOAEL. A benchmark dose analysis was performed by TCEQ staff on the results of this study and BMCL_{10} was determined and used as the Point of Departure (POD) in the calculation of a long-term ESL for this chemical. The long-term ESL determined by this approach was 40 $\mu\text{g}/\text{m}^3$.

Another animal exposure study was identified in the DSD as a supporting study. In that work, rats were exposed for six hours per day, five days a week to 90 ppm of propionaldehyde or for six hours per day for six days to 1,300 ppm propionaldehyde (Gage, 1970). The DSD notes that the description of the results in this study was "very limited", but provides no other explanation why the Gage study shouldn't be used as the Key Study.

The Gage study has two advantages over the Union Carbide study. First, Gage was published in a peer-reviewed journal and Union Carbide was not. Second, the Gage study identified a NOAEL, so it would not be necessary to conduct a benchmark dose analysis with the uncertainty that brings. The NOAEL level of 90 ppm could just as well serve as the POD for an ESL determination.

The two studies used essentially the same protocol and the same species, so the uncertainty factors would be the same as those used in the DSD based on the Union Carbide results. Using the Gage data to establish the POD would result in a long-term ESL of $67 \mu\text{g}/\text{m}^3$, slightly higher than the ESL derived using the Union Carbide results.

By way of comparison, it is instructive to compare the proposed ESLs in this report to occupational exposure guidelines for propionaldehyde. The current American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) for propionaldehyde is an eight-hour average of 20 ppm which is equivalent to $47,400 \mu\text{g}/\text{m}^3$ (ACGIH, 2014).

This TLV was set to protect worker's health when they are exposed to propionaldehyde 8 hours a day, five days a week for a working lifetime. The ESLs proposed in this report are more than 700 smaller than the TLV. While people in the general community may be more susceptible to chemical exposures than workers are, they are not likely to be 700 times more susceptible. Thus the annual average ESL recommended here is quite conservative.

V. CONCLUSIONS AND RECOMMENDATIONS

As explained in this report, the ESL evaluation I conducted showed that for propionaldehyde, a short-term ESL, based on preventing odor nuisances, of $48 \mu\text{g}/\text{m}^3$ and a long-term (health-based) ESL of $67 \mu\text{g}/\text{m}^3$ for propionaldehyde are scientifically supportable. I recommend that these values be adopted as the ESLs for propionaldehyde.

Submitted by:



Dr. Thomas Dydek, PhD, DABT, PE
Consultant for Eastman Chemical Company
Longview, Texas
February 16, 2015

References:

American Conference of Governmental Industrial Hygienists, "Propionaldehyde", in the Documentation of the Threshold Limit Values, ACGIH Worldwide, Cincinnati, Ohio (2002).

American Conference of Governmental Industrial Hygienists, "2014 TLVs and BEIs", ACGIH Signature Publications, Cincinnati, Ohio (2014).

Gage, J.C., "The Subacute Inhalation Toxicity of 109 Industrial Chemicals", British Journal of Industrial Medicine 27:1-18 (1970).

Hazardous Substances Database (HSDB), "Propionaldehyde", data accessed from web site <http://toxnet.nlm.nih.gov/cgi-bin/sis/search> February 2015.

Hellman, T.M. and F.H. Small, "Characterization of the Odor Properties of 101 Petrochemicals Using Sensory Methods", Journal of the Air Pollution Control Association 24(10):979-982 (1974).

Nagata, Y., "Measurement of Odor Threshold by Triangle Odor Bag Method", Odor Measurement Review, Japan Ministry of the Environment, pp. 118-127 (2003).

Lewis, R.J., Hawley's Condensed Chemical Dictionary, Twelfth Edition, Van Nostrand Reinhold Company, New York, New York, page 968 (1993).

National Academy of Sciences (NAS), "Propionaldehyde", accessed February 12, 2015 from http://www.epa.gov/opptintr/aegl/pubs/propionaldehyde_interim_dec_2008.pdf.

Sim, V.M. and R.E. Pattle, "Effect of Possible Smog Irritants on Human Subjects", Journal of the American Medical Association 165(15):1908-1913 (1957).

Texas Commission on Environmental Quality (TCEQ), "Guidelines to Develop Effects Screening Levels, Reference Values, and Unit Risk Factors", TCEQ Publication No. RG-442, http://www.tceq.state.tx.us/comm_exec/forms_pubs/pubs/rg/rg-442.html (2012).

Texas Commission on Environmental Quality (TCEQ), Effects Screening Level list, available on the Toxicology Section's part of the agency's web site the address of which is http://www.tceq.state.tx.us/toxicology/esl/list_main.html#esl_1 (2014a).

Texas Commission on Environmental Quality (TCEQ), Development Support Document for Propionaldehyde, available on the Toxicology Section's part of the agency's web site <http://www.tceq.com/assets/public/implementation/tox/dsd/proposed/oct14/propionaldehyde.pdf> (2014b).

Union Carbide, "Propionaldehyde: combined repeated exposure and reproductive/developmental toxicity study in rats with cover letter dated 04/14/93". Submitted under TSCA Section 8D; EPA Document No. 86, 930000198; NTS No. OTS0538178. Available from the IRIS Hotline at hotline.iris@epa.gov (1993).