Texas Commission on Environmental Quality (TCEQ)

Response to Public Comments Received on the

Proposed Odor ESL Position Paper, *Approaches to Derive Odor-Based Values*, and Proposed Odor ESL List

September 1, 2015

The public comment period for the proposed May, 2015 Odor ESL Position Paper, *Approaches to Derive Odor-Based Values*, and proposed Odor ESL List ended in July 2015. The American Chemistry Council's Center for Advancing Risk Assessment Science and Policy (ACC), Texas Chemical Council (TCC), Arkema Inc., and OXEA Corporation submitted comments. The TCEQ appreciates the effort put forth by these commenters to provide technical comments on the proposed Odor ESL Position Paper. The goal of TCEQ is to protect human health and welfare based on the most scientifically-defensible approaches possible, and evaluation of these comments furthered that goal. A summary of comments from each group is provided below, followed by TCEQ responses. The full comments are provided in Appendices. Comments on issues that suggest a change in the Odor-ESL Position Paper are addressed whereas comments agreeing with TCEQ's approach are not. TCEQ responses indicate what changes, if any, were made to the Proposed Odor ESL Position Paper in response to the comments.

American Chemistry Council's Center for Advancing Risk Assessment Science and Policy (ACC) Comments (See Appendix 1 for details)

Comment No. 1:

Regarding Section 2.0 of the Position Paper, the ACC commented the inclusion of aldehydes and carboxylic acids with sulfides, mercaptans and amines as "chemical groups whose members are most often malodorous" should be qualified. ACC stated that not all of the chemical groups named in the Position Paper are associated with similar negative odor perceptions at all concentrations. Specifically, ACC indicated that not all carboxylic acids and aldehydes are associated with negative odor. In fact, many aldehydes and carboxylic acids are naturally occurring within food and are added to food or as flavorants, and provide desired scent characteristics within foods, cosmetics and fragrances. ACC suggested that the odor ESL values should not descend into the concentration ranges associated with levels found in foods and flavorings that are considered "generally regarded as safe" (GRAS). Odor ESL levels should not be set below levels associated with GRAS. ACC further suggested that the table provided by TCEQ of proposed odor ESLs (May 2015) should delude the current favorable uses of the odors associated with carboxylic acids and aldehydes as well as the objectionable attributes. ACC recommended that the table include concentration ranges used in positive applications and circumstances (within fragrances, foods and flavorings) as well as the concentration ranges that are considered objectionable.

TCEQ Response: The TCEQ appreciates the ACC's comments and agree with the ACC that not all carboxylic acids and aldehydes are associated with offensive odors. As described in the Odor Position Paper, odor-based screening values are not developed for chemicals whose odors are

pleasant unless data are available to indicate frequent odor complaints have been received from facilities emitting these chemicals.

Some carboxylic acids and aldehydes are of strong, offensive odor at high concentration but have pleasing scent at very low concentration. These chemicals have been used as food additives, flavoring and/or fragrant agents. Carboxylic acids often have strong odors, especially the volatile derivatives. Conversely esters of carboxylic acids tend to have pleasant odors and many are used in the perfume industry. The TCEQ is aware that some carboxylic acids such as acetic acid, malic acid, undecanoic acid, lactic acid, and citric acid are widespread in nature. However, the abundance of a carboxylic acid in nature does not alone influence the decision to derive an odor-based screening value. The intended purpose of an odor-based screening value is to evaluate whether predicted or measured concentrations of the chemical of interest originating from an industrial or commercial facility would potentially cause an odor nuisance. Therefore, the primary data sought to inform this decision is focused upon identifying the odor characteristics of the chemical of concern. The goal of a screening value is to prevent chemicals from reaching a level in the environment where they create a nuisance. Given that the ACC presented compelling evidence to suggest that undecanoic acid is not malodorous, the TCEQ has removed this chemical from the Odor ESL List. For carboxylic acids that have a strong odor at high concentrations but have a pleasing scent at very low concentrations (e.g., acetic acid, hexanoic acid, heptanoic acid, octanoic acid, and nonanoic acid), odor ESLs will be developed at higher odor thresholds (i.e., recognition thresholds). The TCEQ is aware that traces of many aldehydes are found in essential oils and are often used for their favorable odors, e.g. cinnamaldehyde, cilantro, and vanillin. The fatty aldehydes (C8-13) also have a very pleasant odor, including fruity or floral scents, that can be detected in very low concentrations. Accordingly, odor ESLs would not be developed for carboxylic acids and aldehydes that lack pungent odor. For example, the proposed odor ESLs list includes only 14 aldehydes although the TCEQ has reviewed available odor thresholds data for 20 aldehydes. Odor ESLs are not developed for cinnamaldehyde, nonaldehyde, decanaldehyde, undecanaldehyde, furfuraldehyde, and benzaldehyde. However, due to the fact that some aldehydes are malodorous at higher concentrations, odor ESLs will be developed at higher odor thresholds (i.e., recognition thresholds) for aldehydes reported to have strong, offensive odor at high concentration but have pleasing scent at very low concentration (e.g., propionaldehyde, butyraldehyde, isobutyraldehyde, and 2-methylpentaldehyde).

Comment No. 2:

Regarding Section 2.0 of the Position Paper, the ACC commended the TCEQ for recognizing the reliable approaches for measuring odor. It, however, commented that the TCEQ should clearly state that if available, data from newer studies using improved methodologies will be used within the data integration exercise rather than older studies. In regard to data integration exercises, ACC recommended that it would be useful to first plot the odor values from the reliable studies and observe the shape of distribution curve prior to selecting the values for the central tendency.

TCEQ Response: The Proposed Odor Position Paper and Odor ESL List were not revised based on this comment. The Odor Position Paper already indicates that data from newer studies using improved methodologies will be considered first. However, a weight-of-evidence approach will be used to evaluate values from these newer studies. Due to improvements in analytical techniques used to acquire data, newer odor-based values may be biased low. This may be

particularly true if the newly identified 50% odor threshold values are significantly below odor values that have historically been used to develop screening values. To assess this possibility, the TCEQ will evaluate whether odor complaints have been received when a previous odor-based screening value was used. In the event that there is no evidence that odor complaints have been received when the older odor value was in use, historical values may be used instead of the newer values that are potentially biased low.

Comment No. 3:
The ACC further recommended that the TCEQ 1) develop a process to evaluate chemical specific information that may be utilized to supersede generic or surrogate odor values; 2) clarify on how the approaches outlined in the Position Paper were used to develop the proposed odor ESLs for the generic categories; and 3) clarify regarding how the TCEQ will determine if the odor ESLs applies or the health-based ESLs applies to chemicals listed without CAS numbers.

TCEQ Response:
The TCEQ appreciates the ACC's recommendations. After review of ACC's comments and similar comments from the TCC and Arkema, the TCEQ reexamined the proposed Odor ESL List and Odor Position Paper. The TCEQ has removed the application of generic, odor-based ESLs for listed chemical classes (sulfides, mercaptans, amines, aldehydes, carboxylic acids, and soluble inorganic fluorides). The Odor Position Paper has been revised accordingly (see Response to Comment No. 11). Therefore, it is not necessary to develop an exclusion mechanism to supersede generic odor values and to clarify on the approach used to develop the proposed odor values for generic categories. The TCEQ has eliminated the generic odor threshold ESLs for listed chemical classes. The proposed Odor ESL List only lists chemicals with pungent, disagreeable odor and specific CAS numbers. However, surrogate odor-based ESLs may be used for chemicals (with or without CAS numbers) with a similar chemical-structure activity to chemicals within same chemical classes.

Texas Chemistry Council (TCC) Comments (See Appendix 2 for details)

Comment No. 4:
The TCC commented that it is unclear why numerous chemicals whose odors are not unpleasant still have ESLs based on odor.

TCEQ Response: As described in the proposed Odor Position Paper, the TCEQ evaluates available chemical specific data, and conducts an analysis to determine whether development of an odor-based value is needed to prevent odor nuisance conditions. A part of that analysis is a review of data describing odor characteristics. If the chemical has reliable data that the chemical has pungent, strong, unpleasant characteristics, an odor-based value is set. Odor-based values will not be developed for chemicals whose odors are considered pleasant. However, odor-based screening values may be developed if historical information indicates frequent odor complaints have been received for a chemical. In addition, as described in Response to Comment No. 1, odor ESLs will be developed at higher reported odor thresholds for chemicals (e.g., some aldehydes and carboxylic acids) that have strong odor at high concentration but have pleasing scent at very low concentration.

Comment No. 5:
The TCC commented that it is inappropriate to apply the generic or surrogate odor threshold of 1 $\mu g/m^3$ to all chemicals in a listed malodorous chemical class. Therefore, it would be useful for the TCEQ to provide a mechanism for chemical-specific information to be considered to supersede these generic values if such data becomes available.

TCEQ Response: See Response to Comments No. 3 and 11.

Comment No. 6:
The TCC recommended that when experimental odor threshold are determined, the odor panel needs to be diverse, with members being randomly selected rather than targeted based on odor sensitivity, so as to mitigate possible biases. Similarly, there needs to be a set of established criteria for panel calibration to ensure each selected member is capable of detecting odors. Many technical elements concerning the use of odor data have been previously submitted (TCC 2009).

TCEQ Response: The proposed Odor Position Paper was not revised based on this comment. As addressed in the 2010 response to comments submitted by the ACC/TCC, this comment highlights an important issue. However, the TCEQ only reviews available odor studies and does not conduct odor testing. Detailed descriptions on odor detection factors and discrepancy of odor perceptions determined under field and controlled conditions can be found in odor reports, such as Guidance for the Application of Odor in Chemical Emergency Response by van Doorn et al. (2002), Assessment of Odor Annoyance in Chemical Emergency Management by Ruijten et al. (2009), and a review of the science and technology of odor measurement by St. Croix Sensory (2005). This particular discussion is considered beyond the scope of the Odor Position Paper.

Comment No. 7:
In comparing the proposed Odor ESL List against the current ESL List, the TCC noted a number of chemicals with decreased odor-based ESL values (i.e. cyclohexanol, methyl methacrylate, hexyl mercaptan, etc.) or no change in ESL values, such as styrene. In addition, the proposed Odor ESL List contains new generic categories such as "mercaptan, generic, not otherwise specified" which comprises the light (up through butyl) mercaptan isomers, some of which have ESLs above 1 $\mu g/m^3$ in the existing ESL List. It is unclear how the proposed odor ESL values were established at lower values than the existing ESL values. Therefore, the TCC requests an explanation on the approaches used to develop the proposed odor ESLs.

TCEQ Response: The proposed odor-based values for cyclohexanol, methyl methacrylate, and diethylamine were incorrect and have been revised to the values listed in the current ESL List [03/17/2014]. As addressed in the TCEQ Response to Comments No. 3 and 11, the TCEQ has removed the generic odor-based ESLs for listed chemical classes (sulfides, mercaptans, amines, aldehydes, carboxylic acids, and soluble inorganic fluorides). It is not necessary to clarify the approach used to develop the proposed odor values for generic categories. For hexyl mercaptan, the current short-term ESL (30 ug/m^3) is health-based. Although there are no odor threshold data available, there is strong evidence that hexyl mercaptan is likely to be malodorous. It is important to derive an odor-based ESL for hexyl mercaptan. Hexyl mercaptan has similar chemical-structure activity to n-butyl mercaptan. Therefore, surrogate odor value for n-butyl mercaptan of 2.7 $\mu g/m^3$ is used for hexyl mercaptan.

Comment No. 8:
Some chemicals are listed without CAS numbers in the proposed Odor ESL List, making it difficult to determine whether the odor-based ESLs apply or the health-based ESLs apply. For example, the "amine generic" category from the proposed Odor ESL List appears comparable to the "process amine solvent" with a CAS No. 132538-98-8 in the existing ESL listing. Please clarify a process on how the TCEQ will determine which ESL List to apply in this case.

TCEQ Response: See Response to Comment No. 3 above.

Comment No. 9:
The proposed Position Paper discusses a variety of chemicals that have several odor threshold values. TCC is not clear on the approaches employed by TCEQ to determine the values established in the proposed Odor ESL List. For example, the proposed ESL values for styrene remain unchanged from the current ESL values when there is evidence in the referenced literature that suggests the short-term ESL value should be 100 parts per billion (ppb) or higher, and not 25 ppb, as listed. Based on professional judgment, it would be expected the ESL for styrene should be increased.

TCEQ Response: The Proposed Odor Position Paper and Odor ESL List were not revised based on this comment. As described in Section 5.0 of the proposed Odor Position Paper, the evidence integration process was employed by TCEQ staff to determine scientifically defensible odor-based screening values using data from a variety of sources for chemicals in the proposed Odor ESL List. With regard to the styrene odor-based ESL, the TCEQ disagrees with TCC's comment that the proposed odor-based ESL should be raised from 25 ppb to 100 ppb. Styrene has been extensively measured in the field and consistently reported by TCEQ's highly trained monitoring staff members or field investigators as causing noticeable and unpleasant smells, nausea and headache at concentrations near the low end of odor detection thresholds range (e.g. 25 ppb). The proposed odor-based ESL for 25 ppb or styrene will assure the prevention of odor nuisance conditions from styrene emissions.

Comment No. 10:
The TCC stated that since new odor-based ESL values are being implemented to assess violations (enforcement actions) not meeting FIDO upon completion of an investigation, it requests consideration be given to the following:

1. The technology used to validate complaints of odors at the less than 10 $\mu g/m^3$;

2. The case-by-case process needs to be changed to allow more company involvement and/or practical risk-based review to ensure enforcement actions that would require significant modification, resources, and capital to comply are assessed based on well-supported data; and

3. The means whereby compliance will be determined or evaluated.

TCEQ Response: The Odor Position Paper was not revised based on this comment. The Toxicology Division acknowledges the TCC's comment; however, the comment is not directly relevant to the proposed Odor Position Paper. The comment is better addressed by the TCEQ Enforcement Division. Therefore, no response is provided by the TCEQ Toxicology Division.

Arkema Inc. (Arkema) Comments (See Appendix 3 for details)

Comment No. 11:

Arkema stated that it supports the detailed comments submitted by the TCC; in particular, TCC's second comment regarding the application of a surrogate odor threshold ESL for listed chemical classes, and a means to supersede these generic odor values. Specifically, it indicated that Arkema manufactures several heavy mercaptans (C8, C9 and C12 alkyl mercaptans) in Texas for which no specific odor-based ESLs have been established, and it would be un-necessarily burdensome to apply the generic threshold in permit authorization evaluations associated with these chemicals. Therefore, as noted in the TCC comment, some exclusion mechanism is needed to avoid the application of an unjustified, extremely conservative ESL. Arkema, however, indicated that an exclusion mechanism, as suggested, could be complicated, difficult to apply consistently, and lengthen the permit authorization process. It further recommended the TCEQ eliminate the surrogate odor threshold ESLs for listed chemical classes and only provide chemical specific ESLs.

TCEQ Response: After review of Arkema's comments and similar comments from the ACC and TCC, the TCEQ reexamined the proposed Odor ESL List and Odor Position Paper. The TCEQ has removed the application of generic odor-based ESLs for listed chemical classes (sulfides, mercaptans, amines, aldehydes, carboxylic acids, and soluble inorganic fluorides). The Odor Position Paper has been revised accordingly. The TCEQ also agrees with Arkema that the current proposed list of odor-based ESLs appears comprehensive and is based on TCEQ's experience with chemicals causing odor complaints. The TCEQ further concurs with Arkema that the proposed list can be expanded as new chemicals are identified as causing odor complaints. The TCEQ believes that such an approach would ensure that each chemical with a pungent, disagreeable odor and its subsequent odor-based ESL is evaluated using the process described in the Position Paper.

No generic odor values will be used for malodorous chemical groups. However, for individual chemicals with reliable evidence they are malodorous, established odor-based ESLs for chemicals with a similar chemical structure to those malodorous chemicals may be used for air permit reviews. For example, an odor-based ESL for valeraldehyde of 99 $\mu g/m^3$ may be used for isovaleraldehyde. Similarly, an odor-based ESL for n-butyl mercaptan of 2.7 $\mu g/m^3$ may be used for hexyl- and heptyl mercaptan. TCEQ toxicologists have considerable expertise in evaluating odor potential for individual chemicals within a chemical group.

The TCEQ has historically considered odor, and its potential to create a condition of odor nuisance, when conducting effects evaluation for air permit applications. As described in the effects evaluation procedure of the MERA guidance document (APDG 5874), case-specific factors such as types of effects, margin of safety, compliance history, and odor complaints will be considered in a Tier III case-by-case review. Odor-based ESLs are guideline levels not

standards. For example, when applying the odor-based ESL in an air permit application review, consideration of the nature of the odor, the surrounding land use, the frequency of odor-based ESL exceedance, and the odor complaint history at the site, all play a role in whether off-site concentrations that exceed the odor-based ESL are allowed.

OXEA Corporation Comments (See Appendix 4 for details)

Comment No. 12:
OXEA commented that the approach to establish odor-based ESLs on the basis of odor detection thresholds (ODTs) alone does not adequately consider the complex process by which odors can produce nuisance conditions. It stated that an approach that incorporates four primary characteristics of odor, i.e., frequency, intensity, duration and offensiveness would be more fit than setting odor-based ESLs simply at ODTs. OXEA specifically commented that propionaldehyde and butyraldehyde have low odor annoyance potential. It proposed alternate odor-based ESLs for propionaldehyde (538 ppb) and butyraldehyde (84 ppb) that incorporate the use of quantitative relationships between odor intensity and concentration for individual odorous chemicals.

TCEQ Response:
The TCEQ appreciates OXEA's comments. As described in Response to Comment No.1, many aldehydes have been used as food additives, flavoring and/or fragrant agents at low concentrations. These aldehydes have strong, unpleasant odor at higher concentrations but have a pleasing scent at low concentrations. The Proposed Odor Position Paper and Odor ESL List have been revised. Odor-ESLs for these aldehydes are now developed at higher reported odor thresholds (e.g. at recognition thresholds).

Both propionaldehyde and butyraldehyde have similar odor character to these aldehydes and have broad range of odor threshold values. Odor ESLs for propionaldehyde and butyraldehyde have been raised from their respective ODT to their respective odor recognition threshold: 40 ppb (92 $\mu g/m^3$) for propionaldehyde and 9.2 ppb (27 $\mu g/m^3$) for butyraldehyde.

The TCEQ acknowledges that use of one times the ODTs as odor-based ESLs may be conservative in the air permitting process. TCEQ staff is aware that several regulatory entities use generic ambient odor standards setting at multiples of the ODT in their air permitting process. The TCEQ is also aware that the National Advisory Committee for Acute Exposure Guideline Levels (NAC/AEGL) set its Level of Distinct Odor Awareness (LOA) for assessing the concentration level for community emergency response activities. ESLs are guideline concentrations for use in TCEQ's effects evaluation of constituent concentration in air. Odor-based ESLs for malodorous chemicals are generally set at one times the ODTs to prevent odor nuisance from multiple facilities (aggregate) in an area that emit the same and/or multiple odorous chemicals (cumulative). As indicated by OXEA, an odor recognition threshold is generally around 3 times the ODT (or even less for odors that are "unpleasant") and may cause offense. As described in the Odor Position Paper, odor concentrations for malodorous chemicals at > 3-5x ODTs or > recognition threshold may indirectly cause health effects. OXEA's proposed alternate odor-based ESLs were calculated at odor annoyance levels which are 60 and 18 times their respective ODTs. The proposed odor ESLs are higher than the upper range of the

Japan Offensive Odor Standards for propionaldehyde (50-500 ppb) and butyraldehyde (9-80 ppb). OXEA's proposed alternate odor-based ESLs for propionaldehyde and butyraldehyde may not prevent potential odor nuisance conditions.

Appendix 1

American Chemistry Council's Center for Advancing Risk Assessment Science and Policy (ACC)

Comments Regarding the TCEQ Proposed Odor ESL Position Paper, *Approaches to Derive Odor-Based Values*, and Proposed Odor ESL List

Appendix 2

Texas Chemistry Council (TCC)

Comments Regarding the TCEQ Proposed Odor ESL Position Paper, *Approaches to Derive Odor-Based Values*, and Proposed Odor ESL List

Appendix 3

Arkema Inc.

Comments Regarding the TCEQ Proposed Odor ESL Position Paper, *Approaches to Derive Odor-Based Values*, and Proposed Odor ESL List

Appendix 4

OXEA Corporation

Comments Regarding the TCEQ Proposed Odor ESL Position Paper, *Approaches to Derive Odor-Based Values*, and Proposed Odor ESL List