Texas Commission on Environmental Quality Response to Public Comments

November 2013 Hydrogen Chloride

Development Support Document

Dr. Thomas Dydek from Dydek Toxicology Consulting submitted comments dated March 7, 2014, on the November 2013 Development Support Document (DSD) for Hydrogen Chloride. The Texas Commission on Environmental Quality (TCEQ) appreciates the effort put forth by Dr. Dydek to provide technical comments on the proposed DSD for hydrogen chloride. The goal of the TCEQ is to protect human health and welfare based on the most scientifically-defensible approaches possible (as documented in the DSD), and evaluation of these comments furthered that goal.

Upon further review, the DSD has been revised. The current $^{acute}ESL_{odor}$ of 10,000 ppb (15,000 µg/m^3) based on a 100% recognition threshold reported by Leonardos et al. (1969) was removed. The proposed $^{acute}ESL_{odor}$ of 60 ppb (89 µg/m^3) measured by van Thriel et al. (2006) was withdrawn. Due to inadequate reliable odor threshold data, an odor-based ESL was not set for the revised DSD.

Comments from Dr. Dydek:

Dr. Dydek submitted detailed comments related to the $^{acute}ESL_{odor}$ only:

> "It is our opinion that there are some methodological shortcomings in the work on which the newly-proposed odor-based ESL was based. This was a study by van Thriel, et al. (2006) . . .

Please refer to Appendix A for Dr. Dydek's complete comments. Upon further review of his comments, the $^{acute}ESL_{odor}$ has been revised, as discussed below.

TCEQ Response:

The TCEQ appreciates and concurs with Dr. Dydek's comments that the validity of this study is questionable. Specifically, he commented that 1) a dynamic rather than static olfactometry is better method for HCL odor test, 2) the exposure level measured at headspace was not well characterized, and 3) the volume of the sniffing bottles used in the van Thriel et al. (2006) study might be too small for sniffs.

The original $^{acute}ESL_{odor}$ of 10,000 ppb (15,000 µg/m3), set in 2009, was based on a 100% recognition threshold reported by Leonardos et al. (1969). However, according to the TCEQ 2012 Guidelines (TCEQ 2012), odor threshold data reported by Leonardos et al. (1969) would not meet Level, 1, 2 or 3 criteria and thus, was removed from the revised DSD. The proposed odor-based ESL for HCl was based on a median odor threshold of 60 ppb (89 µg/m^3) measured by van Thriel et al. (2006). The odor threshold values was determined by static olfactometry

using a two-alternative, forced choice , modified staircase procedure with different concentrations of diluted HCl presented in 280 ml glass sniffing bottle.

Additionally, the odor threshold test employing static headspace dilution may have difficulties in securing a stable and reliable stimulus delivery for odorants with high vapor pressure (Cain et al. 1992 and Cometto-Muniz et al. 2003, as cited in Monse´ et al. 2010). The substantial loss of stimulus strength in sniffing bottle used for static olfactometry may result in poor reliability. A dynamic dilution olfactometry is a better test method (Monse´ et al. 2010). For these reasons and accompanied with Dr. Dydek's comments, the odor threshold value reported by van Thriel et al. (2006) was not used to set $^{acute}ESL_{odor}$ for HCl. Due to inadequate reliable odor threshold data, an odor-based ESL was not set until more research data are available. TCEQ believes that if the health-based ESL of 190 µg/m^3 (130 ppb) is protected, then potential odor nuisance would be protected.

APPENDIX 1

Comments from Dydek Toxicology Consulting

From: Thomas Dydek [mailto:dydek@tox-expert.com]
Sent: Friday, March 07, 2014 4:11 PM
To: TOX; Jong Song Lee
Subject: Comments on DSD for hydrogen chloride

Dear Dr. Grant, Dr. Lee, et al.:

I am writing this message to submit my comments on the newly-proposed Development Support Document for hydrogen chloride. These comments concern only the proposed odor-based ESL. As you know, I have consulted with odor expert Dr. William Cain at the University of California regarding the odor threshold data for HCl. I am basing these comments on the DSD in part on Dr. Cain's input for this project:

It is our opinion that there are some methodological shortcomings in the work on which the newly-proposed odor-based ESL was based. This was a study by van Thriel, et al. in the International Archives of Occupational and Environmental Health (2006). They found an odor threshold for HCl of 60 ppb, which is 167 times lower than the odor-based ESL given in the original (October 8, 2009) DSD for this chemical. Because of the problems with the study in question as outlined below, I think it is premature to change the ESL based on the odor threshold found in the van Thriel, et al. study. More research should first be done to better determine the true odor threshold for this chemical.

One of the weaknesses in the van Thriel, et al. study is that there were two research groups involved. The group in Dortmund performed the work with static olfactometry (stage one; threshold measurements for 15 materials, including HCl) and the group in Bochum performed the work with dynamic olfactometry (stage two; scaling of six materials, not including HCl). So, HCl was studied in the first stage only and it was not studied using the now more acceptable dynamic method. If stage one comprised the only investigation, this might have been enough evidence for accepting the reported odor threshold for HCl, but still with some reluctance. The work in stage two, however, undermined that validity of that in stage one. The group in Bochum used a much better means of stimulus control and delivery. The results led the investigators themselves to question the results of stage one. Specifically, subjects could perceive levels of stimulation that the work in stage one indicated would be imperceptible. The investigators saw the problem and agonized over it to a degree, but did not quite get to the heart of it.

Another shortcoming of the van Thriel, et al. study is that the exposure level was not well characterized. Verification of headspace concentration is still so rare in olfactory research that those who do it normally understand the issues of transfer of vapor to the receptor region. It is unclear from the van Thriel, et al. study about how effectively the stimulus was delivered. There are unanswered questions about whether calibration took place only off line, i.e., only under ideal conditions, and whether there was good control over possible dilution of vapor transferred into the nostril. Off line calibration would presumably not have accounted for any reduction of

concentration from repeated sniffing. Both random and systematic deviations of headspace concentration could occur from repeated presentation of the same vessel.

The volume of the vessels used in the study (280 ml) also is of some concern because "sniffs" are often larger than that. Flow rate is another factor to reckon with. Instantaneous flow rate in a sniff can reach 30-40 liters per minute. If the vessel does not allow for that great a flow or if that is forced through small aperture, transfer of vapor may be compromised or might feel unnatural, i.e., like a blast.

Another question is whether an ESL should be set based on a "calculated" odor threshold. It is possible that van Thriel's own group or the other group (Dortmund) went on to study HCl in the whole body situation that Van Thriel mentions, presumably the same condition as their stage two. If they did that, then they would not present a calculated answer. If, however, Van Thriel chose to look at a factor that would characterize the difference between the glass bottle threshold for other materials vs. his whole body exposure, and then used that factor to adjust the HCl threshold, he would be presenting a threshold that had not been measured, only calculated. This does not seem to be sufficient evidence on which to determine the odor threshold for HCl.

To summarize, with these still unanswered questions concerning the validity of the van Thriel, et al. study, it seems too early to accept their results at face value. More research, either by the group in Germany or elsewhere, would form a much better basis for setting an odor-based ESL for hydrogen chloride.

Please call me at 512-663-7836 to confirm that you have received these comments. Thank you.

Thomas Dydek
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