



# MARY KAY O'CONNOR PROCESS SAFETY CENTER

TEXAS A&M ENGINEERING EXPERIMENT STATION

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21<sup>st</sup> Annual International Symposium  
October 23-25, 2018 | College Station, Texas

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## PHA Guidance for Correlating H<sub>2</sub>S Concentrations in Process Streams to Severity of Adverse Health Outcomes in the Event of a Leak

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**Keywords:** PHA, Dispersion Modeling, Vaporization, Consequences, Health Hazards,  
Hydrogen Sulfide (H<sub>2</sub>S)

### Abstract

Process hazard analysis (PHA) teams are responsible for determining and categorizing the potential impact of a loss of containment. For streams containing hydrogen sulfide (H<sub>2</sub>S), the health and safety consequences of a worker being exposed to H<sub>2</sub>S are a function of airborne concentration in the breathing zone and duration of exposure. PHA teams often do not have the technical knowledge to link the known concentration of H<sub>2</sub>S in the process stream to an adverse health outcome. This paper describes the methodology and the assumptions made in developing such guidance. H<sub>2</sub>S concentration in the stream was correlated to concentration of H<sub>2</sub>S in the breathing zone. Vapor releases used dispersion modeling, while liquid releases required additional modeling to determine the amount of H<sub>2</sub>S liberated from the released liquid. Modeling was done on different process streams under a variety of conditions. Concentration in the breathing zone was linked to the most probable health and safety outcome by surveying relevant literature published by private and government sources. This correlated the stream concentration of H<sub>2</sub>S directly to the consequence categorization used in the PHA. Results were summarized, providing simplified guidance that is valid over a wide range of process conditions and release scenarios.

## 1 Introduction

During a Process Hazard Analysis (PHA) or during incident investigations, teams need to rank the potential adverse health and safety outcomes based on a company's severity scale. This requires multiple steps – first, it needs to be established what the consequence would be; secondly, how it would affect any personnel in the area; and finally, how these effects would be classified per the company's risk standard. For hydrogen sulfide (H<sub>2</sub>S) releases, teams would first need to predict the concentration in the area where personnel are located to determine the potential exposure and then define the effect on a person. That requires knowledge in dispersion modeling and toxicity of H<sub>2</sub>S. This is typically beyond the skill level of a PHA team, thus leaving the team guessing with regards to severity. To achieve comparable risk rankings, it is important that the appropriate severity is determined consistently by different teams.

For risk ranking, the consequence should be based on the most probable worst-case outcome, not the worst possible. When consequences are overrated with regards to severity, it takes attention and resources away from the truly high severity cases. For H<sub>2</sub>S, the hazards of exposure are emphasized in the safety training for anyone working in a refinery environment and there are many well publicized cases of past fatalities. This can lead teams to overestimate the consequences of H<sub>2</sub>S exposure if there are no clear guidelines or data available to help them in their evaluation.

For a qualitative risk analysis, teams can compensate for overstating the severity by understating the frequency – based on the experience that the (overstated) consequence has never been observed. It does not matter for the overall qualitative risk ranking whether the consequence has not occurred because the failure never happened or because the failure did happen but was not nearly as severe as assumed. But when doing a quantitative risk analysis (for example LOPA or QRA), the frequency of the consequence is no longer selected by the team – but rather it is calculated from the probability of the event and the probability of failure of the safeguards. In this case, overstating the severity will result in overstating the risk. Selecting a realistic and most probable worst-case severity is now critical for a consistent risk ranking.

Marathon Petroleum Company, LP (MPC) with support from ABSG Consulting has performed a generalized analysis for predicting H<sub>2</sub>S exposure and has developed guidance for use by risk assessment teams in estimating the probable worst-case severity for exposure in the case of leaks from process equipment containing H<sub>2</sub>S. The following sections detail the methodology and the assumptions that were used to develop the guidance and show the conclusions that were reached based on the analysis.

## 2 Overview

To develop generalized guidance for the severity of H<sub>2</sub>S leaks that is applicable for a wide range of process conditions, dispersion modeling was performed for liquid and vapor streams with a wide range of pressures and H<sub>2</sub>S concentrations. Process conditions were varied between model runs, while other dispersion model parameters used constant values, representing typical conditions. The modeling provided the H<sub>2</sub>S concentration in the air as a function of distance from the leak source for a variety of stream conditions. By selecting a representative distance, this function of distance is reduced to a single value thereby resulting in a direct correlation between stream conditions and H<sub>2</sub>S concentration in the breathing zone of a person (right side in Figure 2-1)

A review of available toxicology data coupled with an assumption for the duration of the exposure linked the concentration of H<sub>2</sub>S in the breathing zone to health effects for an exposed person. These health effects were then classified according to the severity definitions per the company's risk standard. This provided a correlation between exposure and the severity classification (left side in Figure 2-1).

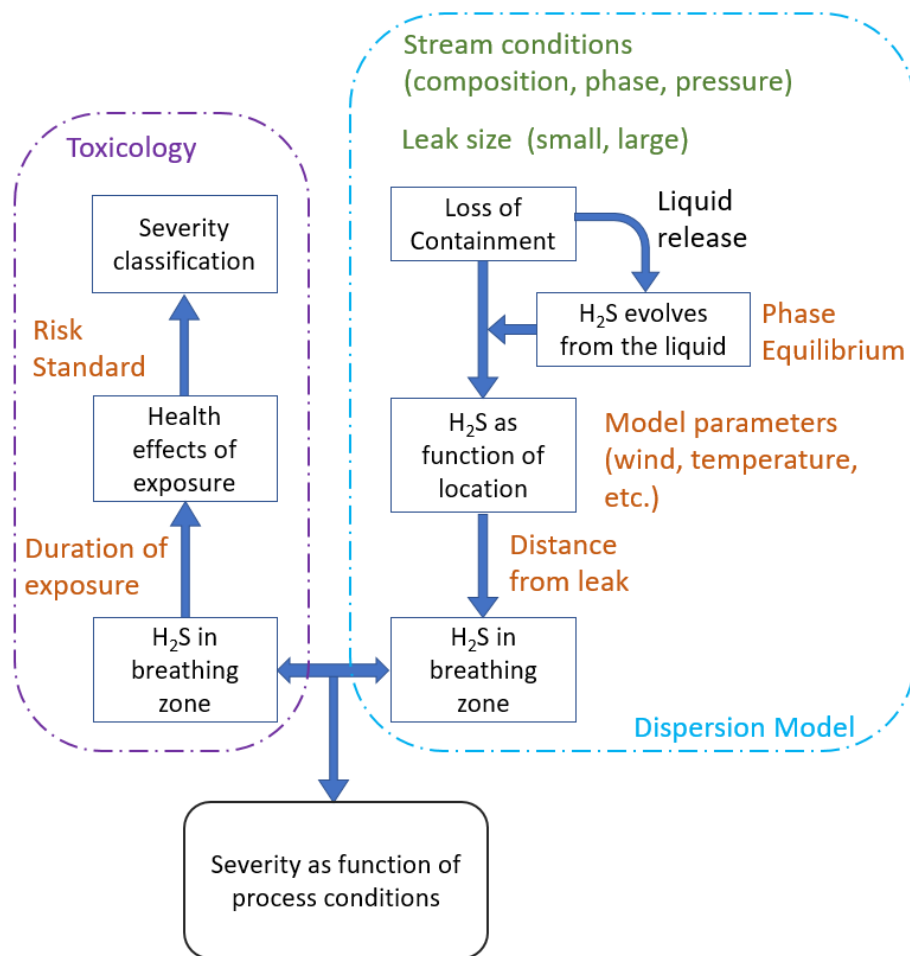


Figure 2-1. Correlating Dispersion Modeling and Toxicology

Combining the dispersion modeling with the toxicology review then allows to directly correlate the stream conditions of the leak with the severity outcome. Figure 2-1 shows an overview of the methodology. Green text in Figure 2-1 indicates inputs to the analysis that were varied. Orange text indicates inputs for which representative values were selected and then kept constant. The steps shown in Figure 2-1 are discussed in detail in the following sections.

### 3 H<sub>2</sub>S Release from Liquid Phase Leaks

The H<sub>2</sub>S concentration in the vapor phase of a release depends on two factors:

1. How much of the material vaporizes upon release; and
2. How the H<sub>2</sub>S partitions into the vapor and liquid phases.

In answering these questions, the released material was broken into categories:

- A. Hydrocarbons containing H<sub>2</sub>S;
- B. Sour Water (contains H<sub>2</sub>S); and
- C. Rich Amine (contains H<sub>2</sub>S).

The fraction of a hydrocarbon that vaporizes upon release depends on several factors including its temperature, pressure, and bubble point. A stream's bubble point pressure relative to atmospheric pressure seems to have the largest effect on how much will vaporize: cold crude may vaporize very little, while hot naphtha may vaporize almost entirely.

Several streams around Crude Units, Hydroprocessing Units, FCCU, and Coking units were studied, specifically looking at streams that contain H<sub>2</sub>S. Hysys, using the Peng-Robinson Equation of state, was used for modeling the phase equilibrium. For many of these streams, about 45% of the hydrocarbon vaporized, to where it is a useful approximation.

These same streams were studied to determine how the H<sub>2</sub>S partitioned. H<sub>2</sub>S is a vapor at standard conditions, so it was not surprising that about 98% of the H<sub>2</sub>S was vaporized, with 2% remaining in the liquid phase. As a simplification, it was assumed that 100% of the hydrocarbon stream's H<sub>2</sub>S is vaporized, which only minimally increases the H<sub>2</sub>S concentration in the vapor phase as compared to a 98% vaporization rate.

The same analysis was conducted for sour water. Under most circumstances, the only vapor generated by the release was H<sub>2</sub>S, and almost 100% of the H<sub>2</sub>S evolved. As a simplification, the PHA team should assume that 100% of the sour water stream's H<sub>2</sub>S is vaporized and that the generated vapor is 100% H<sub>2</sub>S.

This analysis was also conducted for rich amine. Rich amine binds much of the H<sub>2</sub>S, preventing much of it from vaporizing. In the event of a rich amine release, 3% of the amine vaporizes, with 35% of the H<sub>2</sub>S vaporizing.

The hydrocarbon results were used as the basis for the dispersion modeling. The lower H<sub>2</sub>S release from amine was not considered during the remaining modeling. This can result in overstating the severity of rich amine leaks, which was accepted for the sake of simplicity.

## 4 Dispersion Modeling

Dispersion modeling was performed to determine the H<sub>2</sub>S concentrations to which a person may be exposed. The modeling was performed using PHAST (1) software along with spreadsheets and the data manipulation and extraction was performed using FACET3D (2) software.

In the analysis some parameters were fixed constants for all cases and some were variable to capture the range of conditions seen in the field. The below parameters were held constant for all cases in PHAST.

- 5 mph wind speed
- D stability level
- 68 °F ambient temperature
- 70% relative humidity
- 500 W/m<sup>2</sup> thermal flux
- 1 m surface roughness
- Horizontal (non-impinged) release direction
- 3.28 ft release height
- 100 °F stream temperature for vapor cases
- 200 °F flashed vapor temperature for liquid cases
- Instantaneous (Flammable = 18.75 sec) averaging time used when determining downwind concentrations

Parameters which were varied included the stream phase (liquid or vapor), H<sub>2</sub>S concentration in the stream, leak size, and pressure as shown below.

- **Stream phase:** liquid or vapor; liquid streams used N-Hexane and H<sub>2</sub>S while the vapor streams used Ethane and H<sub>2</sub>S
- **H<sub>2</sub>S concentration in the stream:** 25, 50, 100, 250, 500, 1000, 2000, 5000, and 50000 ppm
- **Leak size:** small leaks (0.5 inch) and large leaks (2 inch)
- **Pressure:** low (100 psig), medium (300 psig) and high (500 psig)

### *Vapor Releases*

Vapor releases were straightforward and did not require any post processing other than extracting the H<sub>2</sub>S concentration. Mixtures of H<sub>2</sub>S and Ethane were used in PHAST *Vessel or Pipe Source* models with the *leak* scenario type. The PHAST case list feature was used to build cases with varying parameters. The H<sub>2</sub>S component was tracked explicitly. Results of the dispersion were imported into FACET3D and a script was used to extract the centerline concentration at 3 ft downrange of the release. An example of the H<sub>2</sub>S cloud and the extracted centerline concentration is shown below in *Figure 4-1*.

A distance of 3 ft from the leak was selected to represent the location of a person working on the equipment where the leak occurs (approximately an arm's length plus a wrench's length away). Personnel not working on the equipment, but just passing through the area would likely have a greater distance and thus lower exposure.

### *Liquid Releases*

The expected H<sub>2</sub>S evolution from liquid releases was described above in Section 4. Using those rules, the liquid release modeling in PHAST had the following approach.

1. Determine the liquid discharge rate for the given pressure and leak size.
  - a. An artificially low temperature of 100° F was used such that no flashing occurred in the orifice, maximizing the liquid discharge rate.
  - b. The releases used the same PHAST source models as the vapor cases but with mixtures of H<sub>2</sub>S and N-Hexane.
2. Assume 45% of the hydrocarbon discharge mass turns to vapor and 100% of the H<sub>2</sub>S discharge mass turns to vapor.
3. Create a user defined release in PHAST of just the flashed hydrocarbon and H<sub>2</sub>S vapor. Use the same discharge expanded velocity as the liquid release. Use an expanded temperature of 200 °F (minimum to keep the N-Hexane a vapor for all cases). Use a new mixture of N-Hexane and H<sub>2</sub>S which accounts for the higher H<sub>2</sub>S percentage in the flashed vapor (since 100% of H<sub>2</sub>S flashed but only 45% of the hydrocarbon flashed). In general, this vapor mixture had 2.2 times the H<sub>2</sub>S ppm as the original case description.

Therefore, the final liquid release was modeled as an equivalent vapor release of H<sub>2</sub>S and N-Hexane which represented the flashed hydrocarbons. The dispersion modeling of the equivalent vapor release was performed in the same manner as the pure vapor releases.

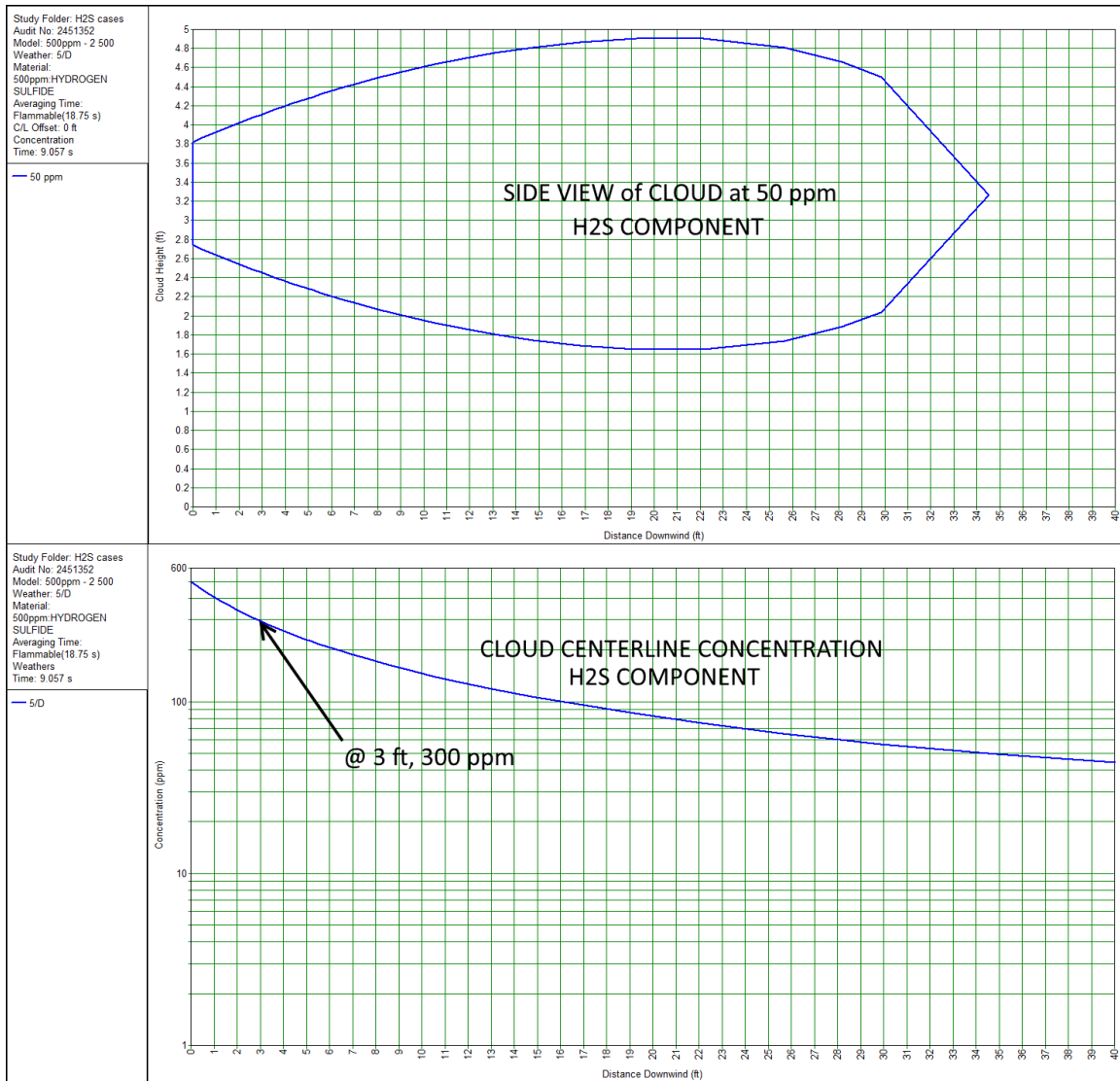


Figure 4-1. Vapor Release for 2" Leak and 500 psig with 500 ppm H<sub>2</sub>S in Stream

### Dispersion Results

Because of the large discharge rates seen in the liquid cases, a larger volume of vapor (H<sub>2</sub>S + hydrocarbon) was released compared to the pure vapor cases. The liquid cases evolved 18% to 42% more vapor depending on pressure. Further, due to the higher concentration of H<sub>2</sub>S in the flashed vapor from liquid cases (since only 45% of hydrocarbon flashed), the resulting H<sub>2</sub>S concentrations downrange were 21% - 44% higher than equivalent pure vapor cases depending on pressure (higher pressures gave higher H<sub>2</sub>S concentrations for liquid vs. vapor releases).

A comparison of the exposed H<sub>2</sub>S concentration vs. the stream H<sub>2</sub>S concentration is shown below in *Figure 4-2*. The following observations are made:

1. The exposed concentration can exceed the stream concentration for the liquid cases since the H<sub>2</sub>S evolves at a higher rate than the hydrocarbon. This is analogous to a distillation

tower which produces a higher fraction of one mixture component at the top compared to the mixture entering the tower.

2. The vapor releases show increasing exposure concentrations with stream pressure while the liquid releases do not. The vapor releases had H<sub>2</sub>S concentrations immediately downstream of the orifice (<1 ft) which were lower than the mixture H<sub>2</sub>S concentration. This effect was larger for lower discharge rate releases. The liquid releases more closely matched the mixture H<sub>2</sub>S concentration at all discharge rates immediately downstream of the orifice. It appears the high velocity vapor releases entrain more air which influences the initial downstream concentrations.

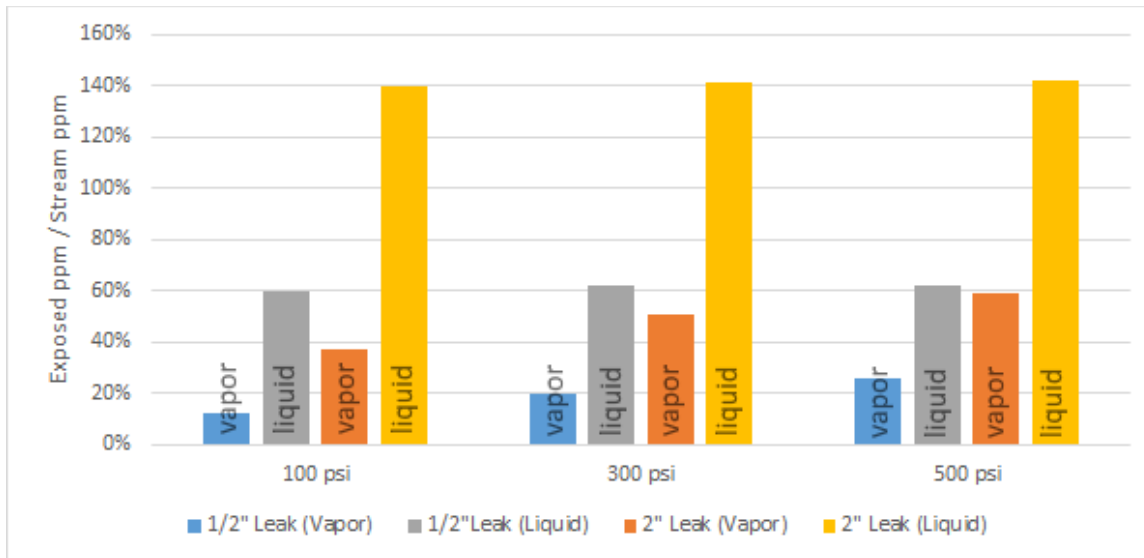


Figure 4-2. Exposed vs. Stream H<sub>2</sub>S Concentration

## 5 Health and Safety Effects of Exposure

Hydrogen Sulfide (H<sub>2</sub>S) is a colorless, flammable gas with a strong, irritating rotten-egg odor. H<sub>2</sub>S is detectable by odor at concentrations significantly lower than those necessary to cause physical harm or impairment. The physiological effects of airborne toxic materials depend on the concentration of the toxic vapor in the air being inhaled, and the length of time an individual is exposed to this concentration. The most serious hazard presented by H<sub>2</sub>S is exposure to a large release from which escape is impacted.

Occupational exposure to hydrogen sulfide is frequently encountered in various industries where H<sub>2</sub>S may be released to the environment as part of the manufacturing/ treatment process. Some of these industries include natural gas production, municipal sewage pumping and treatment plants, landfilling, swine containment and manure handling, pulp and paper production, construction in wetlands, asphalt roofing, pelt processing, animal slaughter facilities, tanneries, petroleum refining, petrochemical synthesis, coke production plants, viscose rayon manufacture, sulfur production, iron smelting, and food processing.



H<sub>2</sub>S and its metabolites are not long-lived in the tissues of exposed animals, indicating that longer-term exposures to low levels may not be as important as short-term peak events. H<sub>2</sub>S is not considered a cumulative toxin since it is rapidly oxidized to sulfate, which is readily excreted in urine.

### 5.1 Animal data (short-term effects)

Results from animal inhalation studies indicate that H<sub>2</sub>S is widely distributed in the body, primarily to the brain, liver, kidney, pancreas, and small intestine (3).

Effect Level mg/m <sup>3</sup> (ppm)	NOEL mg/m <sup>3</sup> (ppm)	Duration of exposure	Effects
35 (25)		Repeated, 3 h/day	Cumulative change in hippocampal type 1 EEG activity in rat
42 (30)	14 (10)	Once for 3 hours	Cytochrome oxidase inhibition in the lung
≥ 70 (≥ 50)	14 (10)	4 h	Inhibition of cytochrome oxidase in rat lung cells
100 (72)		1.5 h/day several	Various cardiac arrhythmias including ventricular extrasystoles in rabbits and guinea pigs
140 (100)		2 h, 4-day intervals, 4 times	Increasing inhibition of cerebral cytochrome oxidase activity and decreased protein synthesis in mouse brain
140 (100)		3 h/day, 5 days	Increased level of L-glutamate in hippocampus of rats
280 (200)		4 h	Detectable histologic lesions in nasal epithelium of rats
280 (200)		4 h	Increase in protein and lactate dehydrogenase in lavage fluids from rat lung
280-560 (200-400)	70 (50)	4 h	Particle-induced oxygen consumption reduced in pulmonary alveolar macrophages from rats
420 (300)		4 h	Marked abnormality in surfactant activity in lavage fluids from rat lungs
560 (400)		4 h	Transient increase in protein concentration and activity of lactate dehydrogenase in nasal lavage fluids or rats
615 (439)		4 h	Transient necrosis and exfoliation of nasal respiratory and olfactory mucosal cells in rat. Reversible pulmonary edema

Table 5-1: Summary of short-term non-lethal studies with H<sub>2</sub>S (4)

## 5.2 Human data (short-term effects)

Separation of effects in humans due to odor nuisance vs. physiological effects is often difficult. Furthermore, most human studies lack the detailed exposure data to derive clear health hazard thresholds.

Effect level mg/m <sup>3</sup> (ppm)	NOEL mg/m <sup>3</sup> (ppm)	Effects
0.028 (0.02)		Minimum perception threshold
0.18 (0.13)		Generally accepted smell threshold
2.8 (2)		Non-significant effects in asthmatic subjects (exposure for 30 min)
4.2-7 (3-5)		Offensive smell
7 (5)	2.8 (2)	Increased muscle lactate levels during exercise (exposure > 16 min) and increased oxygen uptake
14 (10)		Exposure for 15 minutes did not alter the pulmonary function significantly.
14 (10)		Reduced oxygen uptake during exercise (exposure two times 30 minutes)
> 140 (>100)		No smell due to olfactory fatigue
700-1400 (500-1000)		Stimulation of carotid bodies
1400-2800 (1000-2000)		Paralysis of respiratory center and breathing stops

Table 5 -2: Summary of short-term human studies with H<sub>2</sub>S (4)

## 6 Severity Correlation

The health effects of H<sub>2</sub>S exposure detailed in the previous section needs to be related to the severity definitions used in a company's risk standard. For this paper, the severity definitions of "None" through "S4" shown in Table 6-1 were used.

The health effects depend on the duration of the H<sub>2</sub>S exposure – longer exposure leads to more severe effects. For the purposes of the severity correlation, a maximum exposure time of five minutes was used. The value was selected based on the assumption that an exposed person would immediately be alerted to the exposure through their personal H<sub>2</sub>S monitor and quickly evacuate upwind or crosswind once the monitor alarms. Five minutes provides sufficient time for egress even from spaces with limited accessibility.

Table 6-1 lists the severity categories and their definitions used in this paper, as well as the health effects from exposure that correspond to the severity definition and the H<sub>2</sub>S concentration that would cause these effects.

<b>Severity Category</b>	<b>Health and Safety Impact Description</b>	<b>Effects of up to 5 min H<sub>2</sub>S Exposure</b>	<b>Range of H<sub>2</sub>S in breathing zone</b>
Very low / None	No health and safety consequence –	Up to Occupational Exposure Limit (OEL)	0 – 10 ppm
Low (S1)	First aid case	Up to Peak Exposure Limit (PEL); Below US EPA’s 10-min AEGL of 76 ppm; Below AIHA’s 1-hr ERPG-3 of 100 ppm	> 10 ppm to 50 ppm
Moderate (S2)	OSHA recordable incident with no lost time or hospitalization	Loss of smell, irritation of respiratory tract and eyes; Up to IADC’s 300 ppm for 5 min survivability criteria	> 50 ppm to 300 ppm
High (S3)	Injury resulting in lost time, hospitalization or permanent disability	Difficulty breathing, serious eye damage and severe lung irritation	> 300 ppm to 700 ppm
Very High (S4)	Fatality	Rapid unconsciousness, collapse, potentially fatal within minutes due to respiratory paralysis; Threshold of human lethal effect for 10 min exposure (SPEL)	> 700 ppm

*Table 6 -1: Severity Categories*

It is important to keep in mind that this categorization is based on observed effects of exposure and represents a probable worst-case outcome – and not on the worst possible case or an exposure limit. The severity rating is for hazard evaluation purposes only and is not intended to indicate acceptable or safe levels of exposure.

If a company defines the severity levels differently than presented here, the correlation with the health effects and the corresponding H<sub>2</sub>S concentration will need to be adjusted from what is listed in Table 6-1.

## 7 Summarizing the Modeling Results

Each severity category covers a range of H<sub>2</sub>S exposure concentrations. This makes it possible to generalize the results from the modeling because variations in some of the parameters will not cause a significant shift between categories. A sensitivity analysis can indicate which parameters have the most significant effect on the predicted H<sub>2</sub>S exposure and thus the Health and Safety consequences.

Based on the modeling, it was found that the H<sub>2</sub>S concentration in the breathing zone mainly depends on the size of the leak; smaller leaks will result in a lower H<sub>2</sub>S concentration at 3 feet from the leak. Also, vapor releases result in lower H<sub>2</sub>S concentration in the breathing zone than liquid releases with the same H<sub>2</sub>S stream concentration, since the non-H<sub>2</sub>S components in the vapor release dilute the H<sub>2</sub>S concentration in the air. Dependence on pressure was found to be insignificant for liquid releases.

As described in the previous sections, there are many parameters that can affect the analysis, many of which were assumed as constant. For guidance to a PHA team, the results of the analysis need to be simplified and summarized in terms of data that are most readily available to the team. These are generally the conditions of the process stream (available from the material balance for the unit) and the size of the leak. Of these parameters, the H<sub>2</sub>S concentration in the stream, the leak size (small or large) and the phase of the stream (vapor or liquid) have the most significant impact on the severity outcome.

Combining the dispersion modeling results (Section 4) with the severity correlation for breathing air concentrations (Table 6-1) provides a correlation between the release conditions and the health and safety outcome. The following table summarizes the predicted severity outcome for a range of process conditions and leak sizes.

Phase and Leak Size	H <sub>2</sub> S Concentration in Stream							
	25ppm	50ppm	100ppm	250ppm	500ppm	1000ppm	2000ppm	5000ppm
Small Vapor Leak	None	S1	S1	S2	S2	S2	S3	S4
Large Vapor Leak	S1	S1	S2	S2	S2	S3	S4	S4
Small Liquid Leak	S1	S1	S2	S2	S2	S3	S4	S4
Large Liquid Leak	S1	S2	S2	S3	S3	S4	S4	S4

*Table 7-1: Severity Table based on H<sub>2</sub>S Concentration, Leak Size and Phase of Process Stream*

If desired, the guidance can be further simplified by using worst case assumption for the leak size and phase, resulting in a simple table that only requires the H<sub>2</sub>S concentration in the stream as input.

<b>H<sub>2</sub>S Concentration in the Stream</b>	<b>Health and Safety Consequence</b>	<b>Severity</b>
≤ 10 ppm	No consequence	None
> 10 ppm and ≤ 50 ppm	First aid case	S1
> 50 ppm and ≤ 250 ppm	OSHA recordable	S2
> 250 ppm and ≤ 1000 ppm	Injury with restricted duty, lost time or hospitalization	S3
> 1000 ppm	Fatality	S4

*Table 7-2: Simplified Severity Table Based Only on H<sub>2</sub>S Concentration in the Stream*

The simplified severity guidance given in Table 7-2 overstates the severities for small vapor leaks, but results in a simplified correlation for PHA teams that is easy to use. This table can be used as a starting point for the severity estimation. Teams may choose to use the more detailed Table 7-1 if they are concerned that the severity may be overstated or does not match what has been observed in the past, especially if the release comes from a small vapor leak.

## **8 Conclusions**

It is not surprising that estimating the severity of the health and safety consequences of a potential H<sub>2</sub>S release is difficult for PHA teams. The analysis presented in this paper shows the numerous parameters, assumptions, modeling, and toxicity information that is required for this type of estimation. However, by making conservative, but reasonable assumptions for most of these parameters, a generalized correlation between H<sub>2</sub>S concentration in the process stream and the severity of the health and safety effects has been developed.

The generalized correlation provides guidance to PHA teams that is easy to use because it is only based on information that is readily available to them. It helps drive consistency in the severity estimation. PHA teams are often “out of their depth” when estimating consequences and are generally appreciative of clear guidance.

The development of the guidance tables shown in section 7 required multiple assumptions and is based on a specific risk matrix. The values in this table cannot be simply copied from one company to another but will need to be reviewed and adjusted to match each company’s risk standard.

## **9 References**

1. DNV GL, "PHAST," 2011.
2. ABSG Consulting Inc., "FACET3D," 2018.
3. Sullivan and Krieger, 1992.
4. SCOEL. 2007.