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1200 New Jersey Ave., SE
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RE: PHMSA-2014-0099 – Revisions of the Emergency Response Guidebook

The Chlorine Institute (“CI” or the “Institute”) is a 195 member, not-for-profit trade association of chlor-alkali producers worldwide, as well as packagers, distributors, users, and suppliers. The Institute’s North American Producer members account for more than 93 percent of the total chlorine production capacity of the U.S., Canada, and Mexico. The Institute’s mission chemicals, namely chlorine, sodium hydroxide and potassium hydroxide (hereafter referred to as “caustic”) and hydrochloric acid, are used throughout North America’s economy and are crucial to the protection of public health.

PHMSA’s Emergency Response Guidebook (ERG) is regularly used by CI’s members to provide response information for their own emergency response teams, as well as for their local first responders. CI also uses the ERG as a tool in its numerous emergency response training events. The Institute has done a lot of work in the area of emergency response and chlorine release modeling, so we appreciate the opportunity to provide input into the development of the 2016 ERG.

I. Chlorine Release Modeling

A. Summary

The real-world dispersion of a chemical release into the atmosphere is a very complex phenomenon. Every chemical will move and interact with its surroundings differently due to its own unique physical and chemical characteristics. The chemical’s dispersion and the area impacted is also highly dependent upon the specific characteristics of the release source (known as the “source term”), which includes the amount, rate and direction of release, as well as the chemical’s phase upon release (i.e. vapor, liquid, aerosol). Additionally, dispersion is affected by a great number of environmental variables such as ambient temperature, wind direction, wind velocity, moisture (humidity, precipitation, bodies of water), the surface roughness near the release and a host of other components.

With this inherent complexity, all models must make simplified assumptions. It follows that all attempts to exactly model a chemical release via a mathematical algorithm must be only an approximation due to the limitations of the technology. The accuracy of the model’s estimation of cloud dispersion is determined by both the assumptions contained within the model and assumptions made by the user, as well as the accuracy of the input data and parameters used in the simulations.

Data sets from real-world chemical releases are very limited, and for many chemicals, the extensive experimentation and research needed to generate reliable data for atmospheric dispersion is also limited or nonexistent. However, in the instance of chlorine there has been real data generated from chlorine releases.

B. Background

The Jack Rabbit Project (“JR1”), sponsored by the U.S. Department of Homeland Security’s (“DHS”) Transportation Security Administration (“TSA”), was a study designed to improve the understanding of rapid, large-scale releases of pressurized, liquefied toxic inhalation hazard (“TIH”) gases. The project involved outdoor release trials of 1- and 2-ton quantities of chlorine and anhydrous ammonia in 10 successful trials occurring in April and May of 2010. The project was managed by the Chemical Security Analysis Center (“CSAC”), part of the DHS Science and Technology (“S&T”) directorate, and executed at Dugway Proving Ground (“DPG”), a U.S. Army testing installation in Utah. The Chlorine Institute believes that PHMSA should take into account the data and findings available from the chlorine release field trials performed in CSAC’s Jack Rabbit Project in 2010 and apply them to the development of Emergency Response Planning Guidelines (“ERPGs”), as that data represents the most current knowledge of chlorine releases to date.

C. Chlorine Release Behavior

i. Vapor Release

A “vapor release” of chlorine occurs when there is a breach in containment in the headspace (or ullage) of a pressurized tank. When a breach occurs, the pressurized chlorine gas in the headspace of the tank will escape to the outside as a jet of vapor. Once outside the tank, the chlorine vapor will cool as it expands and slump to the ground as a dense gas. If the jet impinges against an object or the ground, frost may be observed forming from condensed humidity on surfaces impacted by the cold chlorine jet.

Inside the tank, the dropping pressure will cause the liquid chlorine to boil, which sustains the escaping jet with additional chlorine vapor. However, the boiling causes the liquid chlorine remaining in the tank to rapidly cool in a process known as “auto-refrigeration.” As the liquid chlorine cools, the boiling will slow and eventually stop once the boiling point has been reached. At this stage, chlorine vapor will be generated at a very slow rate. The liquid chlorine remaining in the tank will be maintained at -29°F (-34°C), and in some cases may remain for hours or days. For breached tanks that have reached an auto-refrigerated state, a frost line can often be observed on the outside of the tank as an indication of the approximate amount and location of liquid chlorine that still remains in the tank.

ii. Liquid Release

A “liquid release” of chlorine occurs when there is a breach in containment at or below the liquid level of a pressurized tank. When the breach occurs, the pressure inside the tank will force liquid chlorine out of the opening, which will immediately flash to a vapor at the exit. Because chlorine liquid is nearly 460 times denser than chlorine vapor, the rate at which chlorine leaves the tank in a liquid release is much greater than a vapor release. A liquid chlorine release for a given hole size will, therefore, generate a substantially larger and more concentrated chlorine cloud at a much faster rate and impact a significantly greater area compared to an otherwise equivalent vapor release.

As the liquid chlorine exits the tank and flashes to a vapor, it will expand greatly and cool down to temperatures near its boiling point. At these low temperatures, the vapor’s density will be

substantially greater than that of air. The resulting cloud will sink toward the ground, typically flow with gravity and the downhill terrain, and accumulate in low-lying areas near the release site, especially under low wind conditions. In other words, the cold, dense gas is held up near the release site and collects in low-lying areas.

Auto-refrigeration will not initially be a significant factor inside the tank during the release, because nearly all of the chlorine's vaporization, expansion, and cooling occur outside the tank. However, once the liquid level drops below the level of the hole, the process takes on the characteristics of a chlorine "vapor release". At this point, the remaining liquid inside the tank will boil and rapidly cool to the point where the contents have been auto-refrigerated, and the vapor will only very slowly be released thereafter.

In some cases involving a chlorine liquid release, escaping liquid may collect in a pool or flow to the lowest level. Generally, liquid chlorine (at -29°F (-34°C)) will boil and rapidly vaporize upon contact with any heat source such as the air, the ground or water. However, as the heat sources surrounding the chlorine pool are cooled, the chlorine's vaporization rate will slow and liquid chlorine can accumulate outside the tank. Pooling is more likely to be observed in releases that involve large quantities, large holes or when the escaping jet impinges against the ground or another object.

D. Chlorine Reactivity/Impact on Dispersion

The Jack Rabbit test data indicated a phenomenon that, to date, has not been utilized in current models dealing with chlorine releases. A key development of the JR1 tests was the quantification of the chemical reactivity of chlorine with soil, vegetation and other organics during a release. As discussed in an article in a recent edition of the *Journal of Hazardous Materials*¹, large quantities of chlorine are removed from a stable plume by deposition. Chlorine deposition positively correlates with moisture and organic matter content and is limited by surface accommodation.

As explained in the article, synthetic soil blends were exposed to dense chlorine ("Cl₂") plumes released during the JR1 tests with the purpose of determining the magnitude of Cl₂ deposition onto soil, as a loss term, and assessing its potential for attenuating a high-concentration plume. Samples were exposed at varying distances from the release point to observe effects of different levels of exposure to the pooling liquid (2–3 meters) and dense vapor (10–17 meters). Following exposure, soil samples were cored, fractionated vertically and analyzed for chloride (Cl⁻) to quantify the integrated amount of Cl₂ deposited. Chloride was detected as deep as four centimeters ("cm") in samples exposed to dense Cl₂ vapor and in the deepest fractions (13 cm) of samples exposed to liquid Cl₂. Chloride concentration, [Cl⁻], in the soil samples positively correlated with soil mass fractions of organic matter and water. While individual contributions to Cl₂ deposition could not be quantitatively determined, the data suggest that organic matter was the primary contributor. [Cl⁻] results from the top vertical fractions (1.3 cm nearest the surface) were used in an analysis to determine the magnitude of deposition as a loss term under low-wind conditions (≤1.6 m/s). The analysis revealed up to 50% of a 1814-kg release could be deposited within 20 m from the release point for soil with high organic matter (43%) and/or water content (29%).

¹ Hearn, John D., Richard Weber, Robert Nichols, Michael V. Henley, Shannon Fox. "Deposition of Cl₂ on Soils During Outdoor Release." *Journal of Hazardous Materials*, Vol. 252-253 (pages 107-114). Elsevier B.V., May 2013. Website: <http://www.sciencedirect.com/science/article/pii/S0304389413001544>

The Chlorine Institute believes that this data has enormous implications for planning, emergency response and mitigation, and that the deposition removal terms for chlorine should be included in future modeling efforts, including the development of the chlorine ERPGs.

II. Practical Use of the ERG for Chlorine Emergency Response

It is very important that the guidelines included in PHMSA's ERG are very clear in their purpose and intent and reflect the most recent data and modeling information so that a more efficient, focused and informed emergency response can be utilized to mitigate the release. In particular, evacuation zone distances and procedures can be refined through improved modeling based on real chlorine release data, such as that resulting from the JR1 tests.

A. Guidelines Based on Modeling Data

When CI reviewed a draft of the 2012 ERG before it was issued, we immediately had concern over the new Table 3 protective action distances, which provides container specific guidance for six TIH materials. Other groups, namely the American Chemistry Council ("ACC") and the Association of American Railroads ("AAR") were also very concerned upon their review of the draft, particularly since they have interest beyond just chlorine. Table 3 was a surprise since these three associations had, in fact, participated in some of the activities to collect information for the 2012 edition to ensure guidelines were based on sound data and real world experiences. As such, the three associations (CI, ACC and AAR) sent a letter to PHMSA's Associate Administrator, Magdy El-Sibaie, requesting a meeting, which occurred on February 16, 2012, to discuss our concerns².

For instance, the 2012 ERG guidance directs a protective action distance of 7+ miles (for large tank car spill, low wind conditions), which is an increase from the general 5 miles included in the previous edition. Preliminary results from the JR1 tests, as well as real world experience, indicated that both of those recommended protective distances were not appropriate, which one can infer are due to modeling uncertainties used as a basis for the guidance. We conveyed this issue to PHMSA during our meeting, but the general response we received was that it was too late in the process to make changes to the 2012 edition. However, we were told our comments would be taken under advisement through the development of the 2016 edition. Therefore, we are taking this opportunity to reiterate the same concerns regarding the protective distances included in Table 3.

Since the 2012 ERG was issued, JR1 test results have been analyzed further and it has become even more apparent that the protective action distances are extremely excessive for what is predicted by the new modeling data.³ Because of the complexity of emergency response events (discussed further in the next section) and the wide distribution and use of the ERG, it is imperative that the information be reliable and based on the best available data.

B. Purpose of Isolation and Protective Action Distances

In addition to using reliable data as a basis for recommended isolation and protective action distances, it is also crucial that the information and purpose of the guidance is clearly understood. CI recommends

² Letter to PHMSA from CI, ACC and AAR dated January 18, 2012 (attached).

³ CI is not at liberty to provide the detailed test results with these comments. However, we encourage PHMSA to contact the Chemical Security Analysis Center (part of the DHS Science and Technology directorate), specifically Dr. Shannon Fox, to review and discuss the Jack Rabbit 1 test results in detail.

that PHMSA include clear definitions for “isolation action distance” and “protective action distance.” It is also important for responders to understand that these are downwind distances suggested for initial on-scene consideration and that all elements of public protection, particularly shelter-in-place, should be considered.

Additional emphasis should be made in the guidebook clearly stating that these distances are not considered a radius, but rather are downwind distances as already described in the book. Also, nothing in the ERG specifies these as evacuation distances, nor should they be. The guidance should be revised to make it apparent that protective action distances should not automatically be considered as evacuation distances. It is a crucial step for the Incident Commander to assess the situation and all of the on-scene factors and conditions involved to determine the appropriate actions and distances.

Should a large scale emergency occur, all parties involved have a responsibility to assure that the appropriate public protective actions are taken to avoid harm. However, if the affected area were to be significantly overestimated (as discussed above) or if extreme or unnecessary protective actions are taken to evacuate hospitals, nursing homes, schools, etc., it would result in a strain in response resources, inconvenience to the public, potential injuries and other unnecessary costs/expenses. Therefore, we urge PHMSA to make the protective action distances well-defined and potential actions well understood.

CI appreciates that PHMSA has provided this opportunity to comment during the development of the 2016 ERG at an early stage. We share PHMSA's goal of preventing hazardous materials releases, as well as ensuring that effective mitigating measures are in place and responders are knowledgeable and trained to reduce consequences for events that do occur. The ERG is an excellent tool for responders to use if they are involved in a hazardous materials transportation incident. CI applauds PHMSA for reaching out to industry for input in an effort for continued improvement and enhancement of the guidance. We are happy to provide further input and assistance throughout the ERG development process, as needed.

Sincerely,



Robyn Kinsley
Director, Transportation