



E X T E R N A L M E M O R A N D U M

TO: U.S. Chemical Safety and Hazard Investigation Board
1750 Pennsylvania Ave, NW, Suite 910
Washington, DC 20006

FROM: Exponent
10850 Richmond Ave., Suite 175
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DATE: December 7, 2017

PROJECT: MGPI Investigation Support - Chemical Reactions and Air Modeling

SUBJECT: Report

Introduction

Exponent was retained by the U.S. Chemical Safety and Hazard Investigation Board (CSB) to provide technical support for their investigation of the incident which occurred at [MGPI Processing](#) in Atchison, Kansas. The CSB Contracting Officer's Representative (COR) transmitted background information to Exponent via email on June 19, 2017, which included the following brief narrative.

During a chemical delivery from a tanker truck, about 4,000 gallons (41,600 lbs) of 30% sulfuric acid was inadvertently connected to a fill line for a sodium hypochlorite tank. The tank contained 5,850 gallons of 12.5% sodium hypochlorite (it was about 90% full). When the sulfuric acid was charged to the incorrect tank, a reaction began, forming a cloud likely containing chlorine gas. Many people described the cloud as green in color.

The reaction went on for about 45 minutes until someone could shut down the transfer. The cloud entered the community and resulted in shelter-in-place and evacuation orders. Over 140 people sought medical attention and some required hospitalization.

The incident involved a chemical reaction of sulfuric acid and sodium hypochlorite. A CSB contractor's chemical analysis report hypothesized a chemical reaction scheme that may have occurred.¹ The resulting chemical products were released into the atmosphere and formed a potentially toxic vapor cloud.

¹ http://www.csb.gov/assets/1/19/2445003_Report_Redacted.pdf

To investigate the constituents that were likely released, the CSB requested that Exponent conduct additional analysis to determine if other notable chemical products than those listed might have been released during the incident, and where they may have been expected to disperse in the atmosphere.

Scope of Work

The scope of services included analysis of the chemical reactions and development of a vapor-cloud dispersion model for the MGPI incident. The analysis evaluated the composition and concentration of the reaction products over time. That data was used to model the dispersion of the product effluents, based on chemical inventories and atmospheric conditions provided for the MGPI incident. The tasks as requested by the CSB, which Exponent undertook, are the following:

Task 1: Evaluate the series of chemical reactions and parallel reactions (if any) that likely occurred during the rapid addition of sulfuric acid into a sodium hypochlorite tank, based on the quantity of reactants and source conditions provided by the COR.

Task 2: Develop a scientifically based approximation of the quantity of chemicals produced from the reaction of sulfuric acid and sodium hypochlorite, based on the quantity of reactants and series of reactions that likely occurred during the incident.

Task 3: Based on atmospheric conditions and additional information about the source and release conditions provided by the COR, use a computational model to calculate the cloud dispersion as a result of the chemical reaction. The model should depict the concentration of toxic reaction products, such as chlorine gas. The computer model should include the following graphical and numerical data outputs: chemical concentration(s) in parts-per-million (ppm) over time; chemical concentration(s) over distance; chemical concentration(s) over elevation; and plume elevation over time.

The plume model results were represented on a Google Earth image, which includes the MGPI facility, overlaid to show the migration of the cloud over time and distance. If applicable, toxic endpoints for the chlorine model should be 3, 10, 50, 400, and 1,000 ppm; toxic endpoints for other hazardous chemicals in the cloud are compared to the IDLH and ERPG-2 values.

Task 1 – Analysis of Chemical Reactions

At the start of unloading of sulfuric acid into the facility's sodium hypochlorite storage tank, the sodium hypochlorite storage tank contained 5,850 gallons of the 12.5% sodium hypochlorite solution. The tank had an operating capacity of 6,500 gallons and a total tank volume of 7,000 gallons. The delivery truck arrived at the facility with approximately 46,160 pounds of 30% sulfuric acid. This truck delivered approximately 41,600 pounds to the sodium hypochlorite tank, with 4,560 pounds remaining in the tanker. The truck was unloaded via a 2-inch diameter unloading hose with a specification for an unloading pressure not to exceed 18 psig. During this filling period, the sulfuric acid reacted with the sodium hypochlorite in the storage tank. The reaction is highly exothermic, with an estimated temperature rise of 72 degrees Fahrenheit, and

some products of the reaction may be gaseous. The evolution of gas from the reactions and liquid added to the tank were released through a 3-inch atmospheric vent and the 18-inch manway lid on the roof of the tank.

Exponent reviewed the information provided to evaluate potential chemical reactions that could occur from the interaction of 30% sulfuric acid and 12.5% sodium hypochlorite solution. The potential reactions outlined in this technical summary may produce toxic gas products and aqueous ionic species. The reaction products identified include the following:

- chlorine gas ($\text{Cl}_{2(g)}$);
- chlorine dioxide ($\text{ClO}_{2(g)}$);
- hydrogen chloride ($\text{HCl}_{(g)}$) or hydrochloric acid ($\text{HCl}_{(aq)}$);
- sodium sulfate ($\text{NaSO}_{4(aq)}$);
- sodium bisulfate ($\text{NaHSO}_{4(aq)}$);
- water; and
- oxygen ($\text{O}_{2(g)}$).

Sodium Hypochlorite Decomposition

In water, sodium hypochlorite forms an aqueous solution of hypochlorite ions (OCl^-) and sodium ions (Na^+). Aqueous sodium hypochlorite is known to degrade over time as a result of the solution's pH, chlorine concentration, solution temperature, light exposure, and impurities if present. From the information reviewed about the event in question, introduction of sulfuric acid would drop the pH of the contents of the tank. The 12.5% sodium hypochlorite solution had an initial pH of 13.² At a pH below 11, the rate of decomposition becomes significant. The reaction between sodium hypochlorite and sulfuric acid is also exothermic, which will further accelerate the rate of sodium hypochlorite decomposition.

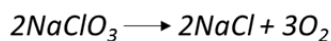
Decomposition leads to sodium chloride and sodium chlorate:³



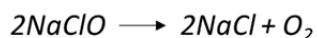
² Vertex Safety Data Sheet.

³ Note that in solution, the reactants and products are present as ionic species.

Sodium chlorate has the potential to further decompose to sodium chloride and oxygen gas:



A minor pathway⁴ of sodium hypochlorite decomposition also leads directly to the generation of oxygen gas:

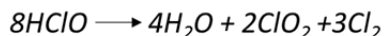


After introduction of the sulfuric acid to the sodium hypochlorite,⁵ the exothermic reaction between the two species would begin.

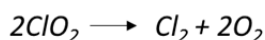
The two reactants have been shown to produce hypochlorous acid⁶ and sodium sulfate.



A potential reaction pathway forming chlorine and chlorine dioxide gas involves direct decomposition of hypochlorous acid:



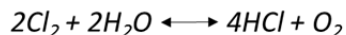
Chlorine dioxide will also react directly with HCl to form Cl_2 and O_2 at temperatures in the range of 40 - 70°C:



Chlorine gas could react with the moisture content in the air or that supplied by the water suppression system to promote the formation of hydrochloric acid and hypochlorous acid in solution.



At high temperature, chlorine gas can react with water to form hydrochloric acid (or hydrogen chloride vapor) and oxygen:



⁴ Sodium Hypochlorite: General Information Handbook, Powell Fabrication and Manufacturing Inc., 2002.

⁵ CAMEO Chemicals, v 2.7, rev. 1, NOAA www.cameochemicals.nao.gov/chemical/4503.

⁶ Bretherick's Handbook of Reactive Chemical Hazards, Vol. 1-2, 7th Edition.

Hydrochloric acid production may further drop the solution pH and produce additional chlorine gas.

Decomposition of sodium hypochlorite is expected to produce hydrogen chloride, chlorine dioxide vapor, and chlorine gas.

Sulfuric Acid Decomposition

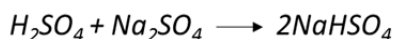
The sulfuric acid delivered to the facility was reported to have a concentration of 30% by weight. Concentrated sulfuric acid reacts exothermically and vigorously with water. Sulfuric acid is a diprotic acid, meaning two hydrogen ions are available for reaction with other molecules. The dissociation of sulfuric acid can proceed through the donation of either one or two protons along the following pathways.



Sulfuric acid can also react at elevated temperature with the sodium chloride in solution to produce sodium bisulfate and hydrochloric acid.



The sulfuric acid could also react with sodium sulfate to produce sodium bisulfate.



Sulfuric acid can decompose to form sulfur dioxide (SO₂), but this decomposition occurs at very high temperatures. Thus, it is unlikely that SO₂ was a significant product of the incident given current information.

Possible reaction products of sulfuric acid mixing with sodium hypochlorite are shown above. The mixing of the two compounds could produce toxic chlorine-containing gases that are consistent in appearance with the greenish-yellow cloud reported by witnesses (see Figure 1).

Task 2 – Estimation of Chemicals Released

The chemical reactions discussed above have the potential to yield toxic products that could cause adverse health effects. During the incident, the reactions described previously were likely dependent on the temperature, concentration, and pH. Given the unknowns surrounding the mixing problem, temperature, and most likely reaction pathways, Exponent conservatively assumed that the sodium hypochlorite might completely decompose during the incident.

Table 1 provides the calculated quantity of Cl_2 that might be produced during the incident. This calculation conservatively assumes that no Cl_2 is reacted or otherwise removed from the cloud in order to estimate a maximum potential extent of dispersion.

Table 1. Mass of chlorine gas (Cl_2) available for release from sodium hypochlorite

Component	Molecular Weight (g/mol)	Moles Available	Mass of Cl_2 Available (kg)	Mass of Cl_2 Available (lb)
Cl_2	70.9	22,310	1,580	3490

Task 3 – Modeling of Toxic Cloud Dispersion

The quantity of Cl_2 listed in the forgoing table is used as the input source term to an air dispersion model to calculate the maximum potential extent of toxic cloud dispersion.

Air Dispersion

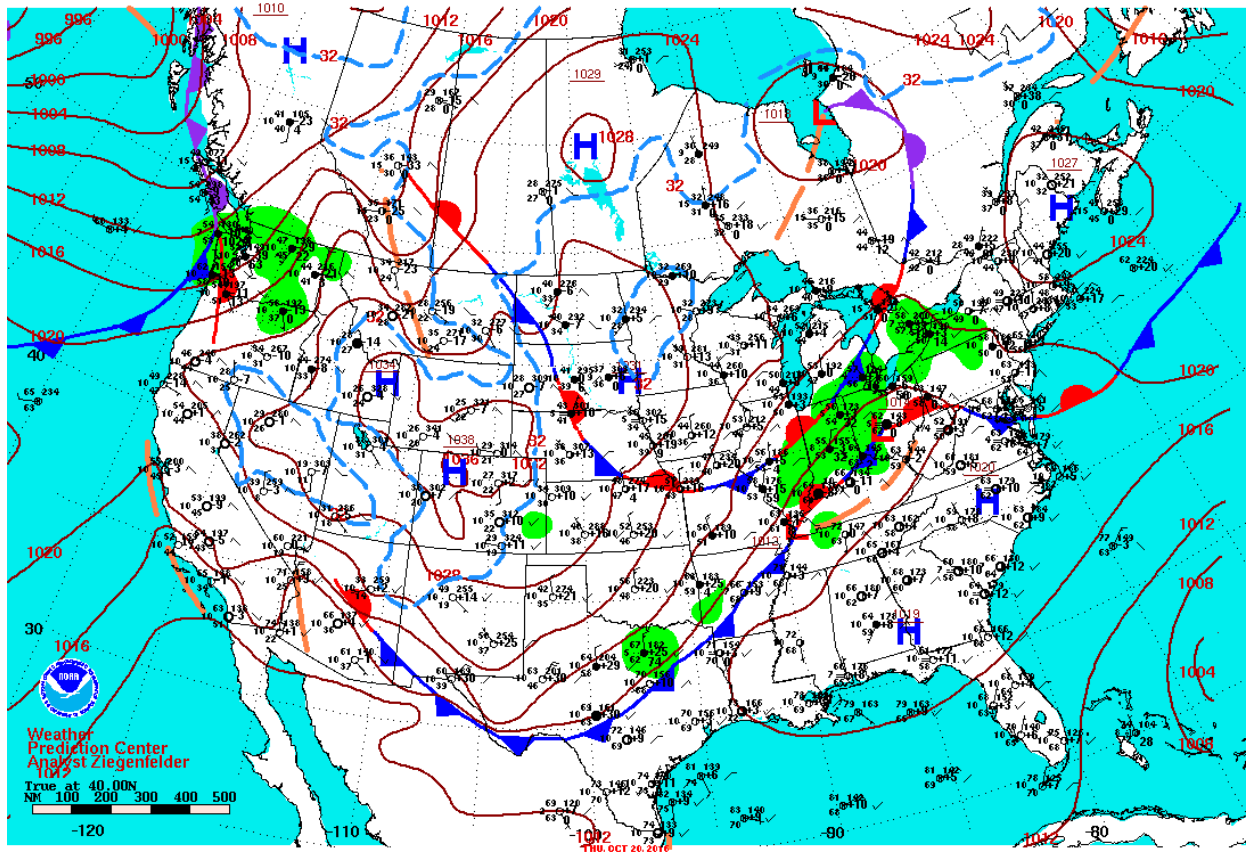
The atmospheric characteristics are necessary for calculating the plume and cloud dispersion. A photograph (attributed to KSHB.com) taken during the event depicts the cloud behavior (see Figure 1). While no time stamp was provided with the image, it shows that the air is stable. The cumuli formed above the exit of stacks appear to form vertically, with little tilt, until a combination of reduced upward momentum and the atmosphere influences the plume to align with prevailing wind at that level. At that height, the winds appear to be significantly stronger than those near the surface are, because the cloud is tilted towards the north.



Figure 1. Release picture taken via a drone, attributed to KSHB.com, and taken by Dunn Heating and Cooling

Shadows in the picture are quite a bit longer than the height of the objects eclipsing the sun that create them, which indicate they represent a time relatively soon after sunrise. Since the sun would appear to rise a bit south of east in late October in Atchison, the shadows are probably lying towards the west northwest. The prevailing wind at the surface is the broad lower cloud, tinged with a yellow-green hue. The remainder of the clouds appear to be white, indicative of reflecting the visible spectrum of sunlight transmitted through the atmosphere. The yellow-green hue in the lower right of the picture is due to reflection of those visible spectral frequencies that are not absorbed or transmitted.

The plume and associated visible cloud seems to generally track along the rail lines from west-southwest before backing to a more southerly component. This counter-clockwise turning of wind with height, referred to as a backing wind, is generally associated with cold air advection and general sinking. This is weather generally ascribed in conjunction with a surface high pressure.



Surface Weather Map and Station Weather at 7:00 A.M. E.S.T.

Figure 2. Archived Synoptic Surface Weather for 6:00 AM CST, October 20, 2016, from the Weather Prediction Center of the National Oceanic and Atmospheric Administration (www.wpc.ncep.noaa.gov).

Synoptic weather maps represent a snapshot of weather conditions at a given time. Figure 2 shows that on October 20, 2016, the day prior to the event, a stationary front appears to be present almost directly over the Atchison, Kansas area. However, during the succeeding 24 hours, as evidenced in the October 21, 2016 synoptic surface weather map seen in Figure 3, this surface feature merged with a cold front ahead of it and together they translated south and east.

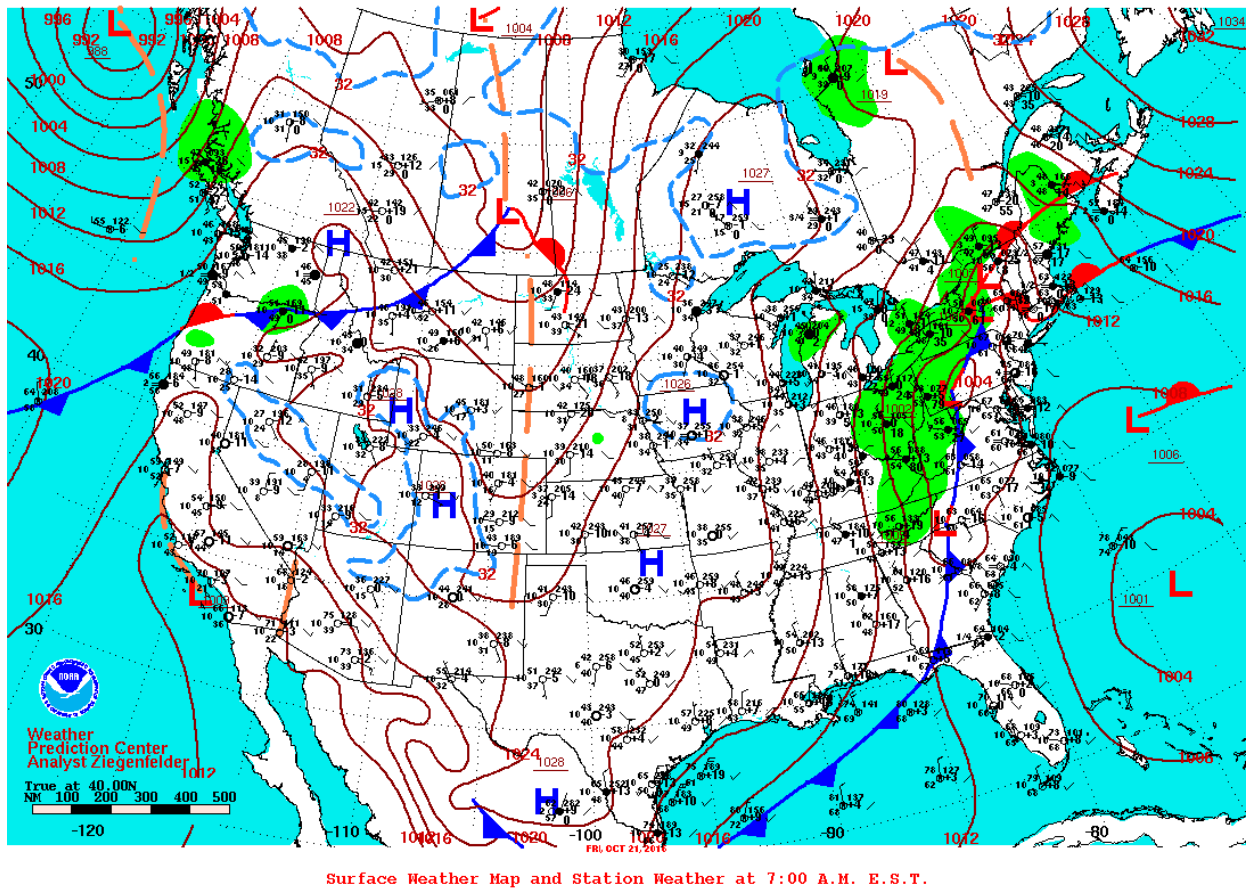


Figure 3. Archived Synoptic Surface Weather for 6:00 AM CST, October 21, 2016, from the Weather Prediction Center of the National Oceanic and Atmospheric Administration (www.wpc.ncep.noaa.gov).

Throughout the release, the Atchison, Kansas area was experiencing high pressure at the surface. A high-pressure ridge, whose axis extends from the Big Bend area of the Rio Grande through the western end of Lake Superior and Arrowhead of Minnesota, is the basis. A relative surface high exists just northwest of the city. Weather conditions associated with this type of event during this time of year include cool, stably stratified, and relatively dry air. Winds are generally very light, especially pre-dawn. Often near the surface, winds are less than a few miles per hour, classified as a calm condition. With light winds, there is often a temperature inversion during the night and early morning where the temperatures increase with height because of cooling via radiation. The strength and depth of the possible temperature inversion layer is unknown, as the stronger the inversion, the more stable the atmosphere.

The high pressure followed in the wake of a low-pressure system that moved through the area over the previous two days. The general surface features advected from the north northwest, steered by the upper level winds.

The closest meteorological reporting stations to Atchison were along the Missouri River, with St. Joseph, Missouri, upstream less than 30 miles and Kansas City, Missouri, about 60 miles downstream. As shown in the two tables that follow, near the time of release St. Joseph was transitioning from fog and calm winds at 7:53 a.m. to fog with winds from the south at 3.5 mph at 8:53 a.m. Kansas City, Missouri conditions were calm up to and including the event. Since the dew point is very close to the actual air temperature at both locations, the relative humidity is quite high. Additional water vapor that evolves and leaves the tank with the dispersing reactants will increase the relative humidity of the ambient atmosphere towards saturation. As the plume rises and cools, the dew point temperature and actual temperature become equal; the air approaches saturation with respect to water and condenses. The upshot is the growing cloud observed in conjunction with this release.

Table 2 Weather History for St. Joseph, MO, October 21, 2016*

Time CDT	Temp (°F)	Dew Point (°F)	Rel. Hum.	Press (in.)	Visibility (mi.)	Wind Dir.	Wind Speed (mph)	Cond.
5:11 AM	37.0	37.0	100%	30.29	0.2	Calm	Calm	Fog
5:53 AM	37.9	37.0	97%	30.30	0.2	Calm	Calm	Fog
6:53 AM	37.9	37.0	97%	30.30	0.2	Calm	Calm	Fog
7:53 AM	37.9	37.9	100%	30.31	0.2	Calm	Calm	Fog
8:53 AM	41.0	41.0	100%	30.32	0.2	South	3.5	Fog

(www.wunderground.com)*

Table 3. Weather History for Kansas City, MO, October 21, 2016*

Time CDT	Temp (°F)	Dew Point (°F)	Rel. Hum.	Press (in.)	Visibility (mi.)	Wind Dir.	Wind Speed (mph)	Cond.
4:54 AM	44.1	41.0	89%	30.29	10.0	Calm	Calm	Clear
5:54 AM	43.0	41.0	93%	30.30	10.0	Calm	Calm	Clear
6:54 AM	43.0	39.9	89%	30.30	10.0	Calm	Calm	Clear
7:54 AM	42.1	39.9	92%	30.31	9.0	Calm	Calm	Clear
8:54 AM	45.0	43.0	93%	30.32	10.0	Calm	Calm	Clear

(www.wunderground.com)*

It is possible that without including orographic effects of the nearby river and surrounding landscape, that the weather Atchison experienced transitioned from calm to slight winds with a southerly component during the release. Using data from these two nearest stations in conjunction with expected weather conditions strongly support the use of low wind speed in very stable air near the surface.

Calm winds have nearly zero wind speed, and the atmosphere was stable. Reactions within the tank are exothermic and provide buoyancy to the hot product gases. In general, these reactants rise as evidenced by the condensation cloud visible above the tank. This plume and visible cloud appear to reach a height where they are neutrally buoyant and then initially spread uniformly away from the imaginary column whose base is the tank opening. Hence, dispersion calculations used a low horizontal wind speed. The minimum recommended wind speed for PHAST is 1 m/s (\approx 2mph). Using this minimum 2 mph with a Pasquill stability class of G provides a relatively large plume that travels downwind with the wind, as shown graphically in the side view graph along the centerline of the plume in Figure 4 from PHAST.

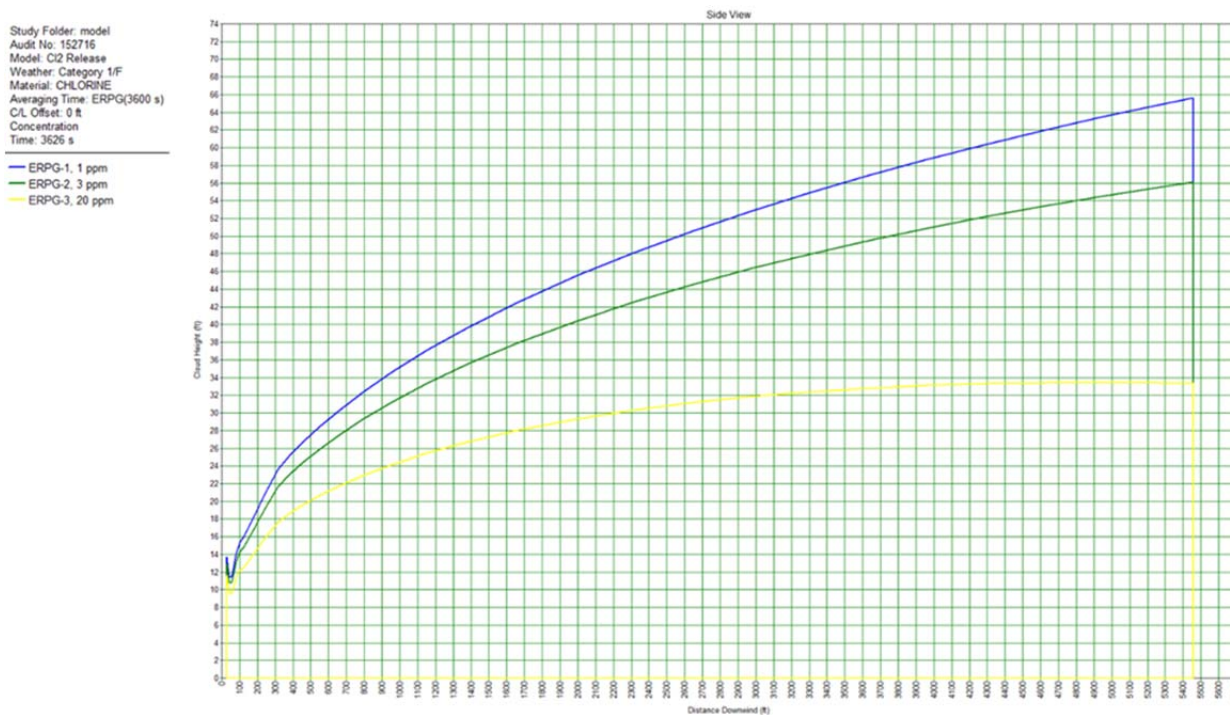


Figure 4. Cloud (plume) side view of chlorine (Cl_2) approximately one hour after release commences along the centerline in direction of wind.

The leading edge in the figure corresponds to the distance an object would travel in 3,626 seconds (approximately 1 hour). Here, at the ERPG concentration and greater, the base of the plume travels along the ground to approximately 5,500 feet.

Note, in Figure 1, the visible portion of the plume is primarily a cloud formed by the activation of cloud condensation nuclei. Water vapor adheres to these liquid water cloud drops, which grow at the expense of water vapor until relative humidity (RH), is reduced to 100%. It is reasonable to assume that the cloud represents a RH of 100%, with lower values outside of that in the plume. Therefore, the calculated plume appears much larger because chlorine dispersed does so in a range of RH, even less than 100%, which is outside the visible cloud. In addition, whatever chlorine is contained within the cloud droplets would tend to reduce the concentration within the plume. PHAST does not permit the chemistry required to see the rate at which the

cloud forms and removes the chlorine from vapor into this aqueous mist. Figure 5, Figure 6, and Figure 7 depict the calculated plume as a footprint when viewed from above it. The concentration outline depicts the extent of the model domain for a given concentration of chlorine at the time of these snapshots. The wind direction was taken to be west southwest, approximately the initial direction of the cloud formed in conjunction with the actual release as seen in Figure 1.

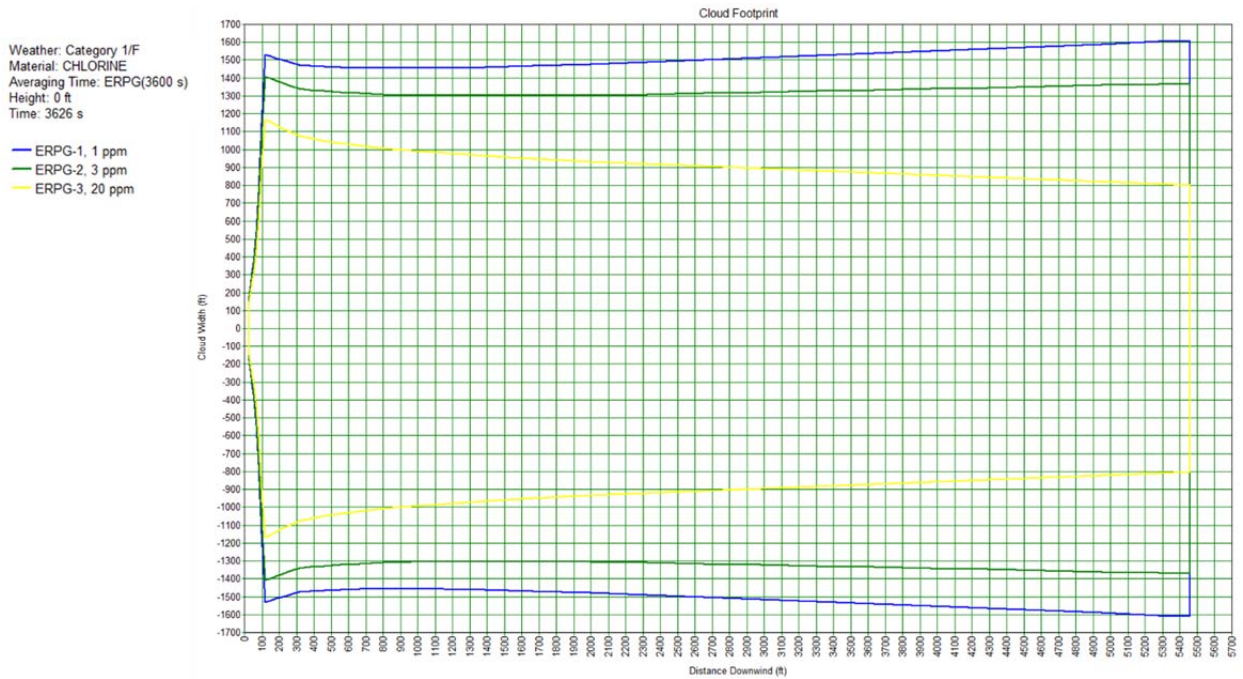


Figure 5. Contours for chlorine ERPG-1, 2 and 3 concentrations at ground level.

Each figure reflects the model results about an hour after the release started into the atmosphere. The ERPG levels in Figure 5 represent concentrations of chlorine gas at 1, 3, and 20 ppm.

Figure 6 depicts the contours for chlorine concentrations of 50 and 400 ppm, and Figure 7 depicts the contours for chlorine concentrations at the IDLH value of 10 ppm.

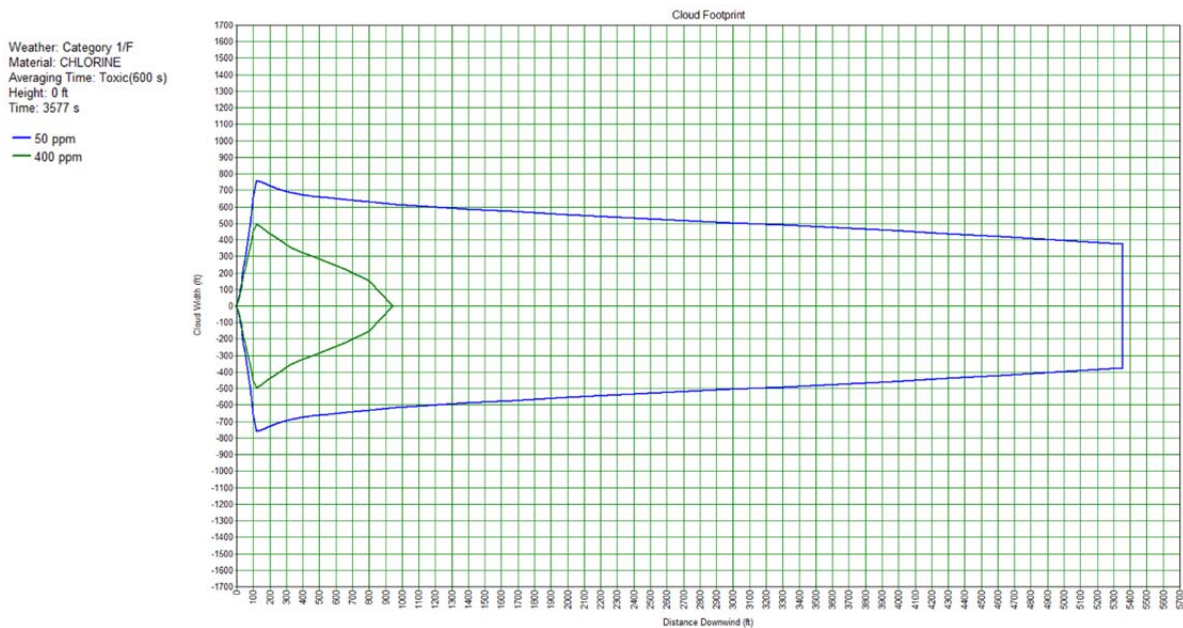


Figure 6. Chlorine Release with concentrations of 50, and 400-ppm levels.

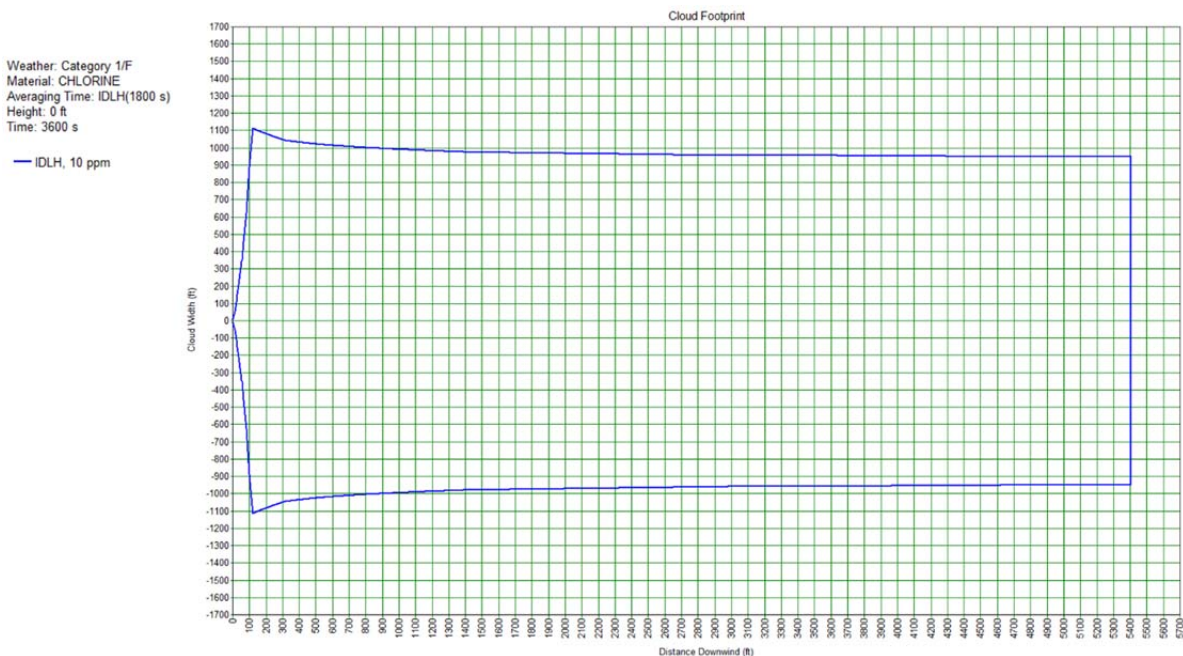


Figure 7. Chlorine release at IDLH (10-ppm concentration)

We did find side reactions that are also important in estimating ranges of products that may arise from the reacting mix and propagate within the plume. These side reaction products may be dispersed separately. However, these constituents are expected to travel with the wind, tracking as does the chlorine gas (Cl_2) and dispersing naturally with distance, with greater efficacy as air outside the plume is entrained to dilute the chlorine and other constituent compounds.

Task 3 Summary

The plume dispersion calculated using PHAST modeling software provides a plume that has some of the basic characteristics of the visible cloud seen in Figure 1. However, it is much larger in extent owing to chlorine concentrations depicted while being dispersed coinciding with water vapor concentrations at less than saturation, i.e., RH less than 100%. Curvature of the dispersed plume with distance downstream and height are not observed using this model owing to its limitations. In addition, no deposition of chlorine with the ground, or removal into cloud droplets is accounted for in the PHAST model.

Secondary side reactions were not modeled owing to the uncertainty in their reaction rate and amount of reactants produced. These reactants would tend to disperse as the chlorine gas does such that total chlorine would be similar. It is recommended to adopt and use more sophisticated software such as Computational Fluid Dynamics (CFD) for dispersion, as well as for better reaction kinetics to see how the constituents behave in the moist plume.

Limitations

At the request of the CSB, Exponent conducted a preliminary investigation of the reactive chemical release incident that occurred at [MGPI Processing](#) in Atchison, Kansas. Exponent investigated specific issues relevant to this incident as requested by the CSB. The scope of services performed during this investigation may not adequately address the needs of other users of this report, and any re-use of this report or its findings, conclusions, or recommendations presented herein are at the sole risk of the user. The opinions and comments formulated during this assessment are based on observations and information available at the time of the investigation. No guarantee or warranty as to future life or performance of any reviewed condition is expressed or implied.

The findings presented herein are made to a reasonable degree of engineering and scientific certainty. We have made every effort to accurately and completely investigate all areas of concern identified during our investigation. If new data become available or there are perceived omissions or misstatements in this report regarding any aspect of those conditions, we ask that they be brought to our attention as soon as possible so that we have the opportunity to fully address them.

Appendix A

Calculations

Chlorine Calculation

The source of chlorine utilized for this study is the sodium hypochlorite (NaOCl). The mass of sodium hypochlorite in the storage tank was reported to be approximately 58,559 pounds. The calculated number of moles based on the pounds reported is shown in Table A-1.

Table A-1 Moles of primary components.

Component	Molecular Weight (g/mol)	Total Mass of Mixtures (lb)	Percentage of Mixture (%)	Mass of Available Components (lb)	Mass of Available Components (g)	Moles
NaOCl	74.4	58,559	13	7,320	3,320,200	44,626

The number of moles of chlorine gas is estimated in pounds for input into the modeling software.

Table A-2 Moles of chlorine gas (Cl₂) available.

Component	Molecular Weight (g/mol)	Moles Available
Cl ⁻	35.45	44,626
Cl ₂	70.9	22,313

Table A-3 shows the mass of chlorine gas (Cl₂) utilized in the modeling software.

Table A-3 Mass of chlorine gas (Cl₂) available

Component	Molecular Weight (g/mol)	Moles Available	Mass of Cl ₂ Available (kg)	Mass of Cl ₂ Available (lb)
Cl ₂	70.9	22,313	1,580	3490

Appendix B

PHAST Inputs

INPUT DATA

Unique Audit Number:

155,189



Study Folder: **model**

Phast 6.7



model



Study

CI2 Release

Base Case

Data

\model\Study\CI2 Release

Material

Material Identifier CHLORINE

Scenario

Building Wake Effect None

Vessel/Tank

Release Type Continuous

Location

Elevation 17 ft
Concentration of Interest 1E-6 fraction
Averaging time associated with Concentration ERPG
Use ERPG averaging time ERPG selected
Use IDLH averaging time IDLH not selected
Use STEL averaging time STEL not selected
Supply a user defined averaging time Not supplied

Bund

Status of Bund No bund present
[Type of Bund Surface Concrete]
[Bund Height 0 ft]
[Bund Failure Modeling Bund cannot fail]

Indoor/Outdoor

Location of release Open air release
Outdoor Release Direction Vertical

Flammable

Jet Fire Method Cone Model

Dispersion

Number of Release Segments 1
Fluid Phase(1) Vapor
Discharge Velocity(1) 3.23 ft/s
Duration of Discharge(1) 3600 s
Final Temperature(1) 110 degF
Release Rate(1) 3490 lb/hr
Pre-Dilution Air Rates(1) 0 lb/hr
Late Ignition Location No ignition location
Mass Inventory of material to Disperse 3490 lb

Fireball Parameters

[Mass Modification Factor 3]
[Calculation method for fireball DNV Recommended]
[TNO model flame temperature 3140 degF]

INPUT DATA

Unique Audit Number:

155,189



Study Folder: **model**

Phast 6.7

Toxic Parameters

[Indoor Calculations	Unselected]
[Wind Dependent Exchange Rate	Case Specified]
[Building Exchange Rate	4 /hr]
[Tail Time	1800 s]
[Set averaging time equal to exposure time	Use a fixed averaging time]
[Cut-off fraction of toxic load for exposure time calculation	0.05 fraction]
[Cut-off concentration for exposure time calculations	0 fraction]

Geometry

Shape	Point
Dimension	2D
System	Absolute
East(1)	808 ft
North(1)	562 ft

[Note: Data in square brackets are defaulted values]