Assessing the Downwind Hazards Associated with Ammonia Release

Executive Summary

We were asked to assess the consequences that would follow a catastrophic release of ammonia from a vessel containing 2,500 tons at the Haifa chemical port and the refrigerated Haifa ammonia tank filled with 4,000 tons of liquid ammonia. We utilized an advanced dispersion model used by the US Department of Homeland Security and Department of Defense in order to instruct our conclusions. Our primary findings are as follows:

1. **Ammonia is one of the most widely used chemicals in the world and has an excellent safety record**
   a. Hundreds of millions of tons of ammonia are transported each year by road, sea and rail
   b. Ammonia's toxicity level is far lower than most other widely used chemicals
   c. In the United States there are 86 ammonia storage tanks comparable to the one at the Haifa port that store over 9,000 tons each.
   d. In the last 22 years there have been only 2 fatalities related to ammonia gas resulting from a breach in any of these 86 tanks
   e. This data shows that for the significantly large US inventory of large ammonia storage tanks there have been no significant accidents at any of them in more than 20 years, save the one major incident (Terra Nitrogen at Sergeant Bluff). This incident , which resulted in a release of 3500 metric tons of ammonia, was due to a breach caused by a nearby ammonium nitrate explosion. Ammonium nitrate (AN) is a common industrial explosive, and have been used in several terrorist attacks, including the 1995 attack in Oklahoma City, OK, USA. Ammonia, in contrast, is not a major explosive hazard, and is lethal primarily through inhalation of the gas/vapor.
   f. Two other highly publicized ammonia tank releases include the 2005 Rostock Germany when a 11,800 ton tank burst, release 105 tons of ammonia, and the Jonova, Lithuania release of 7,000 tons. In both cases, there were no fatalities, either among the workers or the nearby civilian population, and only one serious injury.
   g. The safety record is impressive compared to releases associated with other toxic gases like chlorine, or liquefied natural gas or petroleum derivatives. For instance, incidents involving crude oil, and fatalities involving crude oil have increased since 2010, including a crude oil fire in 2015 in Quebec, Canada, which killed 47 people.

2. **A vessel carrying 2,500 tons of refrigerated liquid ammonia into the Haifa port poses no significant risk to public safety.**
   a. The worst case breach has a risk zone of 400 meters

    b. The public receptors are over 1.5 km away from the source of the release
    c. The only people exposed to the risks of the release work in and around the port industrial area and are likely equipped and trained to manage this risk

3. **The ammonia tank in Haifa holding 4,000 tons of refrigerated ammonia poses no significant risk to public safety.**
    a. The integrity of the tank as discussed in the Stress Engineering Services report of 2015 certifies the tank's excellent condition and expected life of 55 more years
    b. The tank's unique two concrete walls surrounding it ensure that in any breach the spilled ammonia will pool and lead to a very slow evaporation with low concentration levels
    c. Our estimate is that the worst case breach of the tank with 4,000 tons has a risk zone of less than 400 meters, far short of any residential community
4. **The risk estimates provided by the group of professors related to the Haifa tank used a risk assessment model that is completely inapplicable for ammonia**
    a. The model utilized by Professor Ehud Keinan, called ALOHA, is widely known to be a simple to use model that is not applicable for a gas that is lighter than air
    b. Since ammonia is lighter than air and rises rapidly when it is released it is completely inappropriate to use ALOHA to predict its behavior.
    c. The model we utilized, SCIPUFF, is designed to accurately forecast the behavior of lighter than air gasses by taking into account the movement of the cloud up as well as out.
    d. Using the wrong model impacts risk zone distances by 10x and the assessment of populations at risk by hundreds of thousands of people. This could lead to incorrect and irresponsible conclusions.

Overview

In order to analyze the true risk of fatalities from an Ammonia release in the Haifa area, we studied the impact of Ammonia releases under a variety of conditions. We utilized a complex model called SCIPUFF which is used by the US Department of Homeland Security (DHS) and Department of Defense (DOD) in order to accurately predict the risks associated with toxic chemical attacks and spills. The SCIPUFF model takes into account many variables such as buoyancy and wind change that the more rudimentary ALOHA model does not. The impact of these variables on the behavior of an ammonia release leads to materially different results, and making decisions based on the behavior of an ammonia release using a model like ALOHA results in misleading and incorrect conclusions. Utilizing the SCIPUFF model we determined the risks from a catastrophic event on a refrigerated ship carrying 2500 tons in two tanks or a refrigerated tank on shore holding 4000 tons is very limited. **The results define a risk zone of less than ½ km from the point of release not reaching any significant residential areas.**

The results from this study show that downwind effects, when using state of the art Lagrangian [1] based atmospheric transport and dispersion (AT&D) models, generate very limited downwind plumes for even a very large, catastrophic Ammonia release. Sensitivity studies show that credible downwind plume from a release from a transport ship (2500 metric ton) results in lethal dosages that will be less than 200 meters to maximum of 300 meters. Results for the 4000 metric ton, land based storage tank show credible plumes to 300-400 meters downwind.

Key conclusions then are:

1) Credible source scenario – We provide justification for assumptions regarding realistic credible release scenarios from the shipboard storage tanks and the on-land storage tank. The rationale is similar to that used in the 1974 US Coast Guard (USCG) report on ammonia accidents on ships. Thus, in Haifa, the possible releases of ammonia to the atmosphere are much less than the total mass in the storage tank.

2) Further, the buoyant effects of ammonia are so dramatic, that the state-of the-art models are essential to account for this behavior.

3) Ammonia absorbed in sea water – We use the 1974 USCG report to demonstrate that over half of the ammonia released from the shipboard tanks that drains onto the surface of the sea water is absorbed and any ammonia that is released more than ½ meter below the surface is essentially fully absorbed. This significantly reduces the amount of ammonia gas released to the atmosphere.

4) Liquid ammonia constrained in donut shaped ring around large ammonia tank – The ammonia gas evaporative emission rate at the large storage tank is minimized by the fact that the liquid is constrained in a relatively small area between the outside of the tank and the inner concrete wall surrounding the tank. It should be remembered that there is a second concrete wall surrounding this structure, as well as a concrete enclosed bund area, providing triple levels of containment of any liquid ammonia release.

5) The ammonia gas that is emitted from the liquid pool is always more buoyant than the ambient air and will result in the plume rising to heights of several hundred meters, thus greatly reducing ground-level concentrations. This plume rise effect is accounted for by

SCIPUFF but not by ALOHA. This explains why ALOHA was erroneously predicting very long hazard distances (it kept the plume at the ground all the time).

Background

Over the past several months, there have been serious concerns raised about the potential for high numbers of fatalities from the release of large quantities of ammonia in and around Haifa. The issues addressed focus on the potential release of large volumes of Ammonia. While Ammonia is not the most toxic hazardous substance transported, it is the most widely transported toxic industrial chemical in the world, based on a 2010 study conducted by the U.S. Transportation Security Agency [2]. As such, it is absolutely critical to understand the fundamental properties of ammonia, its behavior, and the conditions that affect it, and therefore the impact that a large instantaneous or continuous release might have.

Ammonia is a high volume toxic chemical with an annual production exceeding 11million tons in the U.S, and over 140 million tons worldwide. It is commonly used in at least 10 different industries, including household cleaning, building materials, pesticides, fertilizers, refrigeration, among others. Both ammonia liquid and vapor are irritating to the skin, eyes, and respiratory tract. According to the U.S. Transportation Security Administration [3], it is the highest transported tonnage of toxic industrial chemical in the U.S. (see chart at right).

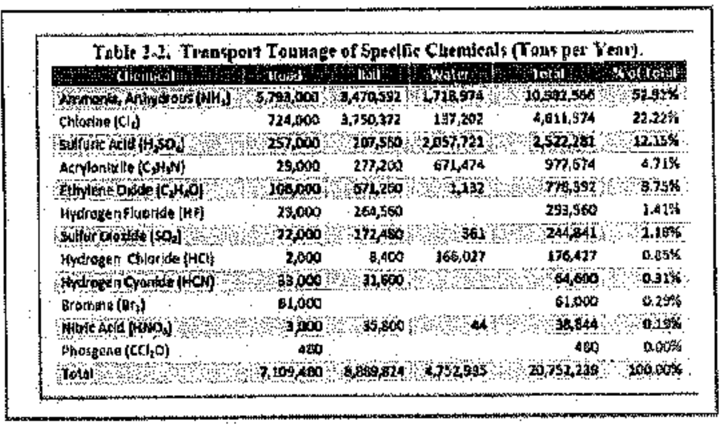
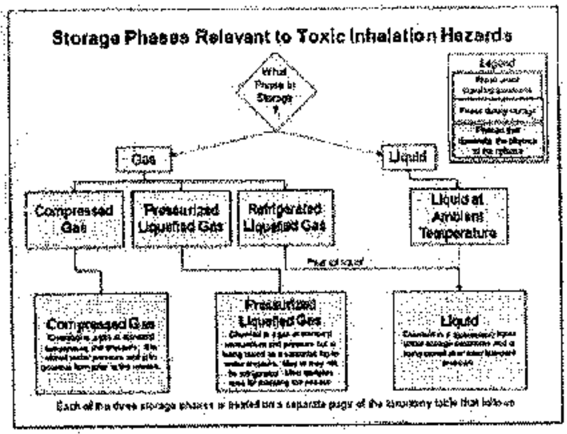


Table 1-1. Transport Tonnage of Specific Chemicals (Tons per Year).

Chemical	Road	Rail	Water	Total	% of Total
Ammonia, Anhydrous (NH_3)	5,793,000	3,470,592	1,718,974	10,982,566	52.92%
Chlorine (Cl_2)	724,000	3,750,372	137,202	4,611,574	22.22%
Sulfuric Acid (H_2SO_4)	257,000	207,560	2,057,721	2,522,281	12.15%
Acrylonitrile (C_3H_3N)	29,000	277,200	671,474	977,674	4.71%
Ethylene Oxide (C_2H_4O)	108,000	671,260	1,132	778,392	3.75%
Hydrogen Fluoride (HF)	29,000	264,560		293,560	1.41%
Sulfur Dioxide (SO_2)	72,000	172,480	361	244,841	1.18%
Hydrogen Chloride (HCl)	2,000	8,400	166,027	176,427	0.85%
Hydrogen Cyanide (HCN)	33,000	31,600		64,600	0.31%
Bromine (Br_2)	61,000			61,000	0.29%
Nitric Acid (HNO_3)	3,000	35,800	44	38,844	0.19%
Phosgene (CCl_2O)	400			400	0.00%
Total	7,109,400	8,889,824	4,752,935	20,752,238	100.00%

Ammonia is a colorless gas with a pungent odor, which causes irritation and burns in the respiratory tract, chest pain, nausea and vomiting. Although ammonia, under ambient conditions, is a gas/vapor, anhydrous ammonia is normally transported under conditions that make it a liquid. It is either transported as pressurized liquid at ambient temperature or as a chilled liquid at -33C and no pressure. It should be noted that Haifa Chemicals Ltd has most of their ammonia transported using the latter set of conditions. This includes ship based, pipeline and large tank storage. Accordingly, any release/spill from any of these containers would necessarily



require it to be treated as a liquid release followed by boiling/evaporation. The chart at the right highlights this, and is highlighted in a 2009 report by the Institute for Defense Analysis on the evaluation of dispersion models. [4] If ammonia is released from pressurized liquid storage containers, it forms a two phase mixture that can be denser than air for a period of time, due to the presence of aerosol drops. This phenomenon was identified in the Jack Rabbit I field trials in 2010 conducted by the DHS Chemical Security Analysis Center [5]. However, the ammonia transport and storage to and in Haifa is not pressurized, and will not exhibit this dense gas behavior.

Because the toxicity of ammonia is often raised as a key point in restricting it use or introduction, a direct comparison to other common toxic chemicals is useful. Table 1, below, highlights the relative toxicity of ammonia compared to other common toxic industrial chemicals and toxic inhalation hazards based on the median lethal dose (LCT_{50}). The LCT_{50} is defined as the dose necessary to kill ½ of the target/experimental population. The table goes from the most toxic materials at the top, to the lesser toxic ones at the bottom. As can be seen, ammonia is less toxic than many of the commonly used industrial chemicals and solvents, including carbon tetrachloride, anhydrous hydrogen chloride, bromine, and chloroform. Ammonia clearly does not approach the toxicity levels of some of the very dangerous chemicals, such as phosgene, hydrogen cyanide, or even methyl isocyanate.

Table 1. Toxicity Values of Common Toxic Industrial Chemicals From Most Toxic (at top) to Least Toxic (at bottom)

Chemical	LCT50
	mg-min/m^3
VX	30
Phosgene	1500
Methyl isocyanate	2250
Hydrogen Cyanide	2500
Hydrogen Sulfide	7000
Arsine	7500
Chlorine	9500
Bromine	27940
Phosphine	44200
Chlorform	93700
Carbon Tetrachloride	122900
Carbon Monoxide	195800
Hydrogen Chloride	200000
Hydrogen Fluoride	280000
Ammonia	300,000
Toluene	750000
Chlorobenzene	750000
Hexane	750000
Acetaldehyde	750000

Taking this into consideration then, this paper addresses the primary concerns associated with the delivery and storage of ammonia at the Haifa Port. To do this, we consider several potential scenarios:

a) Hazard associated with breaching a ship carrying 2500 metric tons of ammonia.
b) Hazard associated with breaching a 12000 metric ton land based storage tank containing 4000 metric tons of ammonia.

Atmospheric transport and dispersion (AT&D) modeling is employed to examine the immediate and downwind hazard associated with prescribed plausible worst case scenarios. In order to employ AT&D modeling, however, several considerations must be taken into account:

a) The use of the best current estimates of Ammonia toxicity
b) The use of the most relevant AT&D model/software

Both of these considerations are discussed in the following sections.

Best and Appropriate Ammonia Toxicity Estimates

Estimating Accurate Doses

The dose, and consequently the effect, of a chemical to which a person is exposed is a function of the concentration of the chemical, the route of exposure, and the time/duration of the exposure. For a toxic industrial chemical like Ammonia, inhalation is the most relevant means of exposure. For inhalation, there are two common equations used to determine dose: Haber's Law [6] and the Toxic Load model [7].

The most often used method is Haber's Law, which is simply the product of the concentration and the time exposed:

$$K=C \times T$$

Experiments with laboratory animals have shown that Haber's Law does not apply to many toxic chemicals. Given the same dose, the effect of exposure is often found to be more severe for short exposure durations than longer ones. As such, these experiments have shown a nonlinear dependence with respect to chemical concentration. This relationship, known as the Toxic Load model is:

$$T_p = C^n \times (t_f - t_i)$$

Where $T_{e,p}$ is the toxicological effect in the specified percentage of the population, n is the toxic load exponent, t_f is the final time and t_i is the initial time. If $n > 1$ then this normally signifies that high concentration, low duration events will produce more toxic effects. For time varying concentrations, two implementations of the toxic load model have been proposed, the ten Berge implementation [8], and the mean Concertation implementation [9].

The ten Berge [10] implementation of the Toxic Load model is

$$K=C^n \times T$$

Where n is the toxic load exponent. The value of n differs for each chemical, and is determined through concentration vs. time experiments. When $n < 1$, the length of exposure has a greater effect on the dose than the concentration. When $n>1$ (most frequently found for the majority of toxic industrial chemicals), the concentration (C) has a greater effect than time (T). For $n=1$, Haber's law is followed, with time (T) and concentration (C) having equal weight. For ammonia, the toxic load exponent (n) has been found to be 2 [11], meaning the toxic load expression is:

$$K = C^2 \times T$$

This suggests that populations closest to the release location may receive a higher toxic load than those further away. However, this unequal distribution may create major differences between the Haber and ten Berge implementations in fatality estimation. For toxic load exponents greater than one, Haber's Law overestimates longer range, lower concentration doses. It is therefore critical to use the Toxic Load model when examining longer range plumes and estimating dose.

The ten Berge implementation is difficult to incorporate into many models, so an approximation if used:

$$TD = D * \left(\frac{T}{T_{ref}}\right)^{\frac{1-n}{n}}$$

Where D is the actual dose, T is the exposure time, n is the toxic load exponent, set at 2 for Ammonia, and T_{ref} is a reference duration. This equation permits the use of LCT numbers (explained below) directly, although this approximation tends to overestimate exposure at low duration times (the most common occurrence for acutely toxic chemicals) and underestimate for longer exposure times.

Estimating Potential Fatalities

When estimating potential casualties associated with exposures, then lethal concentrations, as developed from toxicological investigations, must be used. This is the technique used by many U.S. Government Agencies when conducting calculations to estimate potential fatalities. LCT_x is the lethal dose for a given population percentage (x). Therefore an LCT_{50} is the dose necessary to kill 50% of the population (median lethal dose), LCT_{01} is the lethal dose necessary to kill 1% of the population, etc.

For examining action distances associated with emergency planning and response operations, acute exposure levels (AEGLs) [12] are useful. AEGLs are used by emergency planners and responders worldwide as guidance in dealing with rare, usually accidental, releases of chemicals into the air. AEGLS are expressed as specific concentrations of airborne chemicals at which health effects may occur. **AEGL values were not developed to predict casualties; applying them as such drastically overstates the effect.** Identifying casualties based upon AEGL [13] levels is inappropriate to predict the realistic consequences of an ammonia release.

For the purposes of this investigation, we are using the following parameters:

Toxic Load exponent (n): 2

Toxicity of Ammonia [11]
LCT01: 82,747 mg-min/m^3
LCT05: 93,815 mg-min/m^3
LCT10: 100,309 mg-min/m^3
LCT50: 127,017 mg-min/m^3
LCT90: 160,837 mg-min/m^3

Acute Exposure Guidelines [13]
AEGL-3 (30 min): 1600 ppm
AEGL-3 (10 min): 2700 ppm
AEGL-2 (10 or 30 min): 220 ppm

Definitions for each of the AEGL levels are [12]:

AEGL Level	Definition
1	Notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
2	Irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
3	Life-threatening health effects or death to the most at risk populations

Available Models/Software

There are a number of models and software implementations for atmospheric transport and dispersion (AT&D) available today, either free or at cost. It is beyond the scope of this paper to describe these in detail, but the major models are shown in Table 2. A description of each of these models is provided in the Appendix.

Comparison of ALOHA and SCIPUFF AT&D Models

For the purposes of this study, we have conducted a series of calculations with the advanced SCIPUFF modeling system [14] for releases of ammonia from a transport ship with a maximum capacity of 2500 tons. Because this type of ship does not utilize a single ammonia storage tank, but rather two tanks, a catastrophic release of all of the ammonia is highly unlikely. Consequently, only a fraction of the total amount of ammonia on the ship would be released in a given event. Therefore, as previously stated, in order to properly assess the potential impact that either an instantaneous or continuous release might have, it is absolutely critical to understand the fundamental properties of ammonia, its behavior and the conditions that affect it, so the event may be properly modeled / simulated. Similarly, the modeling program must contain the mathematical, thermodynamics, and behavioral characteristics of ammonia and have the capability for analyzing a robust range of meteorological and geographical conditions.

The SCIPUFF model is being used instead of ALOHA for 5 primary reasons:

1. ALOHA relies on rudimentary inputs that are intended to be used by first responders to define approximate concentration limits of the release. As such, complex parameters that could vastly change the expected results, are not included. SCIPUFF uses a much more complex series of inputs which will generally yield a more comprehensive and realistic result.
2. ALOHA utilizes basic scientific equations and principles that date back 40-50 years. SCIPUFF has been continually updated, and the algorithms utilized are considered "state-of-the-art" for transport and dispersion models.
3. ALOHA is limited in its ability to adequately include or represent source term configurations. As has been seen in recent outdoor tests [5], how the compressed or cooled liquid exits the tank is essential to accurate characterization and prediction. As such, an accurate depiction of these source terms is the single most important aspect of generating realistic plume behavior. SCIPUFF is able to represent a wide range of release conditions and source terms, meaning that less approximation is required and a much better representation of the actual release can be envisioned.
4. Terrain has been shown repeatedly to have a major impact on both the meteorological conditions and the movement (and concentration) of the cloud/plume. ALOHA does not have the capability to include any terrain features, which in many cases, could make the results quite problematic. SCIPUFF's terrain capability provides the ability to represent some key features, which permits an inclusion of deviations of wind flow and plume movement.

5. Likewise, SCIPUFF includes a much better representation of meteorological parameters which are essential for adequately representing both the source term and the resulting plume.

Scenarios Considered

There are essentially two potential scenarios that are relevant to a large scale, ship based release of ammonia. The first, which has generated a large amount of interest over the past few decades due to accidents and collisions, is the rupture of the tank below the vapor/liquid interface in the tank, either above or below the water line of the ship. The second scenario considered the importance to pressurized liquefied storage, and is a breach in the vapor space of the tank, with the liquid ammonia boiling off rapidly at first, until the temperature in the tank drops to below -33C. Because the tanks in the ship are refrigerated at -33C and at roughly one atmosphere of pressure, the ammonia will be liquefied and there will be no effect from the boiling/vapor release inside the tank, resulting in a pure ammonia vapor plume. Due to the relatively small amount of vapor evaporating in the second secnario, the first scenario was considered the "worst case" for a ship-based release.

With respect to the first scenario, in 1974, the US Coast Guard published a report on the behavior of up to a 3000 ton release in and on water [15]. Due to the significant maritime bulk transport of liquid anhydrous ammonia in refrigerated (-33C) ambient pressure tanks, the USCG explored the behavior and effects of liquid ammonia on and in water. Key conclusions from this report include:

a. Ammonia released at depth below the water surface does not result in substantial vapor generation.
b. A short term temperature rise and increase in pH in the water at the release site is observed.
c. Approximately 60% of the ammonia released on the surface is dissolved or reacted with the water, and does not vaporize.
d. The vapor is very buoyant, and rises into the air rapidly and dispersing, as it travels downwind.

Results

The specific scenarios explored for the shipboard release in this paper are shown in table 3 below. Because the ammonia is stored in 2 tanks aboard ships, scenarios explore the release from one or both tanks. In addition, based on the above mentioned USCG report, most scenarios considered employ the 60% reduction due to reaction/solvation. Model input wind speeds and direction are varied in sensitivity runs, as is the ambient temperature. The 2500 ton ship based scenarios described here also considers that both tanks rupture simultaneously, although in reality, a simultaneous release is unlikely. Even a 30-40 second delay will result in a significant decrease in the resulting plume concentration and length. Therefore, this simultaneous release does represent a "worst case" set of circumstances. All input parameters, including wind speed, direction, and temperature, were identified in consultation with HAZMAT, Inc.

Table 3: Ship based Scenarios

Scenario No.	Type	Amount	Type of Release	Amount Released (Tons)	Wind Speed (m/s)	Wind Direction	Ambient Temp (°C)
1	2500 ton Ship	2 Tanks	Surface	1100 (1)	1.5 Stab: F	To the SW	10
2	2500 ton Ship	2 Tanks	Surface	1100 (1)	1.5 Stab: F	To the SE	10
3	2500 ton Ship	2 Tanks	Surface	1100 (1)	3 Stab: D	To the SW	25
4	2500 ton Ship	2 Tanks	Surface	1100 (1)	3 Stab: D	To the SE	25
5	2500 ton Ship	1 Tank	Surface	520 (1)	1.5 Stab: F	To the SW	10
6	2500 ton Ship	1 Tank	Surface	520 (1)	1.5 Stab: F	To the SE	10
7	2500 ton Ship	1 Tank	Surface	520 (1)	3 Stab: D	To the SW	25
8	2500 ton Ship	1 Tank	Surface	520 (1)	3 Stab: D	To the SE	25
9	2500 ton Ship	2 Tanks	Surface	1100 T(1)	10 Stab: D	To the SW	25
10	2500 ton Ship	2 Tanks	Surface	1100 (1)	10 Stab: D	To the SW	25
11	2500 Ton Ship	2 Tanks	Surface	2500	10 Stab: D	To the SW	25

(1) From USCG "Prediction of Hazards of Spills of Liquid Ammonia on Water", 1974.

The results of these scenarios are shown in the table 4 below. Distances for AEGL-3 levels (10 minute and 30 minutes values), and LCT01 and LCT90 contours are provided, and were visually determined as the maximum length from the release point to the edge of the appropriate contour. Only the three scenarios (9, 10, and 11) with wind speeds of 10 m/s show the greatest distances of plume extension. However, even considering these worst case scenarios, including scenario 11, which removes the USCG assumption of 60% removal of liquid ammonia, the plumes travel less than ½ km. This shows clearly that these parameters, with the exception of wind speed, have little or no impact on the size or concentration of the resulting plume. Further, by overlaying the resulting plumes onto Google Earth™, one sees that all of the plumes are limited to either over water or in industrial areas of Haifa. The plumes do not extend to residential areas in any of the scenarios. Table 4A, at the end of this report, combines tables 3 and 4.

Table 4 : Resulting Plume Distances for 2500 ton Ship Releases

Scenario No..	AEGL-3 (10 min) Distance (meters)	AEGL-3 (30 min) Distance (meters)	LCT01 Distance (meters)	LCT90 Distance (meters)
1	170	150	150	130
2	160	160	160	140
3	170	160	150	140
4	160	150	140	110
5	150	140	100	70
6	120	120	110	90
7	120	120	110	95
8	110	110	100	90
9	300	220	190	140
10	280	215	140	125
11	400	300	300	250

Similarly, six scenarios identified in table 5 were considered for the fixed, land-based storage tank. For these scenarios, a catastrophic breach results in the liquid ammonia pouring out into the areas between the tank and the concrete walls, creating a narrow, deep pool. Because of the requirement of SCIPUFF, the liquid pool surface is assumed to be at the top of the concrete tank wall and at ground level. The rate of evaporation of this pool is then evaluated in accordance with the state-of-the-art pool evaporation algorithms.

Table 5: Storage Tank Scenarios

Scenario No.	Type	Wind Speed	Wind Direction	Ambient Temp
12	4000 ton container	1.5 Stab: F	To the SW	10
13	4000 ton container	1.5 Stab: F	To the SE	10
14	4000 ton container	3 Stab: D	To the SW	25
15	4000 ton container	3 Stab: D	To the SE	25
16	4000 ton container	10 Stab: D	To the SE	25
17	4000 ton container	10 Stab: D	To the SW	25

Distances, similar to those described above are:

Table 6: Storage Tank Plume Distances

Scenario No.	AEGL-3 (10 min) Distance	AEGL-3 (30 min) Distance	LCT01 Distance (meters)	LCT90 Distance (meters)
12	140	170	350	220
13	170	190	350	220
14	230	280	360	270
15	260	300	380	290
16	270	300	280	200
17	260	290	260	180

As can be seen in the resulting distances, the results are similar to the ship release case, although the higher winds, including the 3 m/s wind speed (scenarios 14 and 15) do result in longer plume distances as well. The lack of a real downwind hazard is due to two factors: 1) this is predominantly a liquid release at -33C, the plume is caused only by evaporation; and 2) ammonia is very buoyant with most of the vapor rising instead of traveling downwind.

These calculations show dramatically shorter distances than most previous calculations. This is primarily because ALOHA, as described in the online technical manual [16], does not account for buoyancy effects or plume rise. To explore this and to attempt to understand why there is such a divergence in the distances, we compared a similar scenario using ALOHA, SCIPUFF with the correct ammonia buoyancy, and SCIPUFF with neutral buoyancy. The results are shown in Table 7 below.

Table 7: Plume Results for Non-Buoyant/Buoyant Scenarios

Scenario No.	Type	Amount	Type of Release	Amount Released (Tons)	Wind Speed	Wind Direction	Ambient Temp	AEGL-3 (30/60 min) Distance
18	ALOHA	2500 tons	Pool	2500 Tons	3 m/s	SE	25	4000*
19	SCIPUFF (buoy)	2500 tons	Pool	2500 Tons	3 m/s	SE	25	400#
20	SCIPUFF (non-buoy)	2500 tons	Pool	2500 Tons	3 m/s	SE	25	4000#

*60 min AEGL-3 #30 min AEGL 3

The buoyancy effects, or rather, the lack of accounting for buoyancy appears to be the major reason the SCIPUFF results are much more realistic and shorter. When SCIPUFF is run without buoyancy effects, and using similar release and meteorological conditions, the results are consistent with the ALOHA distances. It is well documented that the "lighter than air" positive buoyancy effects must be accounted for. The results here show roughly a 10X difference between effect distances going from buoyant to non-buoyant. Overlaying these reduced plumes onto population densities will result in reduced fatalities estimations, possibly much greater than a 10X reduction.

Screen captures of SCIPUFF generated plumes for selected scenarios are provided in Figures 1-4. Figure 1 (scenario 1) provides a "baseline" picture. Figures 2 and 3 (Scenarios 10 and 11) use the same parameters except for the removal of the USCG correction term. Figure 4 (scenario 20) shows the dramatic and unrealistic effect of removing ammonia buoyancy effects. The curves depicted in each of the figures are lethal doses, as represented by LCT01, 10, 50, and 90 contours.

The specific dosages represented are:

LCT01:	82,747 mg-min/m^3	LCT05:	93,815 mg-min/m^3
LCT10:	100,309 mg-min/m^3	LCT50:	127,017 mg-min/m^3
LCT90:	160,837 mg-min/m^3		

Summary/Conclusions

The results generated by the calculations conducted in the study show that downwind effects, when using state of the art Lagrangian-based AT&D models, generate very limited downwind plumes for even a very large, catastrophic Ammonia release. Key conclusions then are:

1) Credible source scenario – We provide justification for assumptions regarding realistic credible release scenarios from the shipboard storage tanks and the on-land storage tank. The rationale is similar to that used in the 1974 Coast Guard report on ammonia accidents on ships. Thus, in Haifa, the possible releases of ammonia to the atmosphere are much less than the total mass in the storage tank.

2) Further, the buoyant effects of ammonia are so dramatic, that the state-of the-art models are essential to account for this behavior.

3) Ammonia absorbed in sea water – We use the 1974 report to demonstrate that over half of the ammonia released from the shipboard tanks that drains onto the surface of the sea water is absorbed and any ammonia that is released more than ½ meter below the surface is essentially fully absorbed. This significantly reduces the amount of ammonia gas released to the atmosphere.

4) Liquid ammonia constrained in donut shaped ring around large ammonia tank – The ammonia gas evaporative emission rate at the large storage tank is minimized by the fact that the liquid is constrained in a relatively small area between the outside of the tank and the inner concrete wall surrounding the tank. It should be remembered that there is a second concrete wall surrounding this structure, as well as a concrete enclosed bund area, providing triple levels of containment of any liquid ammonia release.

5) The ammonia gas that is emitted from the liquid pool is always more buoyant than the ambient air and will result in the plume rising to heights of several hundred meters, thus greatly reducing ground-level concentrations. This plume rise effect is accounted for by SCIPUFF but not by ALOHA. This explains why ALOHA was erroneously predicting very long hazard distances (it kept the plume at the ground all the time).

Bibliography

[1] S. A. f. a. description.

[2] SAIC Prepared for CSAC, "Modeling Large Scale Toxic Chemical Releases Gap Analysis," 2010.

[3] J. Aherne, *Private Communication.*

[4] Institute for Defense Analysis, *Evaluation of Transport and Dispersion Modeling,* 2009.

[5] *Jack Rabbit I was conducted by the Chemical Security Analysis Center at Dugway Proving Ground in 2010. 1 and 2 ton quantities of ammonia were released from presuurized cylinders to examine the near field effects..*

[6] G. DW, "The use of Haber's law in standard setting and risk assessment," *Toxicology,* pp. 17-19, 2000.

[7] S. D. C. S. Sweeny LM, "Impact of non-constant concentration exposure on lethality of inhaled hydrogen cyanide.," pp. 205-16, Mar 2014.

[8] W. ten Berge, A. Zwart and L. Appleman, "Concentration-Time Mortality Response Relationship of Irritant and Systematically Acting Vapors and Gases," *Journal of Hazardous Materials,* vol. 13, p. 308, 1986.

[9] L. A. B. J. G. J. L. L. Weinrich SL, "A Comparative Analysis of Toxicity Models," Institute for Defense Analysis, 2008.

[10] W. ten Berge, A. Zwart and L. Appleman, "Concentration-Time Mortality Response Relationship of Irritant and Systematically Acting Vapors and Gases,"," *Journal of Hazardous Materials,* p. 306, 1986.

[11] C. S. B. B. P. K. Sommerville DR, "Review and Assessment of Ammonia Mammalian Lethality Data and the development of a Human Estimate," Chemical Security Analysis Center, 2010.

[12] "https://www.epa.gov/aegl/about-acute-exposure-guideline-levels-aegls," [Online].

[13] Environmental Protection Agency, "Compiled Acute Exposure Guideling Values," 2016.

[14] "For a descriiption of SCIPUFF see www.sage-mgt.net," [Online].

[15] A. D. Little, Inc, "Prediction of Hazards of Spills of Anyhdrous Ammonia on Water," Prepared for the U.S. Coast Guard, 1974.

[16] "Areal Locations of Hazardous Atmospheres Technical Documentation Version 5.4.4," 2013.

[17] "from www.scipuff.org," [Online].

"I, the undersigned, George R. Famini, PhD, have been requested by__Haifa Chemicals, Ltd_ to provide the court with this written opinion as an expert in the following questions related to the physical and chemical behavior of ammonia. This written opinion is provided by me in lieu of a personal testimony in court and I have been made aware that according to the provisions of the criminal law regarding perjury, the legal standing of this written opinion, when it has been signed by me, is as the legal standing of a testimony under oath in court."

George R. Famini, PhD

I, the undersigned, Dr. Steven R. Hanna, have been requested by Haifa Chemicals, Ltd to provide the court with this written opinion as an expert in the following questions related to the physical and chemical behavior of ammonia. This written opinion is provided by me in lieu of a personal testimony in court and I have been made aware that according to the provisions of the criminal law regarding perjury, the legal standing of this written opinion, when it has been signed by me, is as the legal standing of a testimony under oath in court.

Steven R. Hanna, Ph.D.

I, the undersigned, Ian Sykes, PhD, have been requested by Haifa Chemicals, Ltd to provide the court with this written opinion as an expert in the following questions related to the physical and chemical behavior of ammonia. This written opinion is provided by me in lieu of a personal testimony in court and I have been made aware that according to the provisions of the criminal law regarding perjury, the legal standing of this written opinion, when it has been signed by me, is as the legal standing of a testimony under oath in court.

R. F. Sykes

Ian Sykes, PhD

Dr. George R. Famini

Dr. Famini recently retired from the Department of Homeland Security. He possesses thirty five years of experience in exploring the science and technology surrounding toxic chemical threats and hazards, and in developing countermeasures to those threats. Dr. Famioni created and led the DHS Chemical Security Analysis Center, and established it as the premier laboratory for studying the effects of toxic chemical threats to the American homeland. He is recognized as a national and international expert in assessing the risk and threat associated with toxic chemicals, and in characterizing those threats. Dr. Famini is also recognized for applying computational chemistry to understanding and characterizing chemical properties and behavior. Dr. Famini has published over 80 journal articles and 300 technical reports on the threats and risks associated with hazardous chemicals.

Dr. Steven Hanna

Dr. Hanna is a specialist in atmospheric turbulence and dispersion, in the analysis of meteorological and air quality data, and in the development, evaluation, and application of air quality models. He is an AMS Certified Consulting Meteorologist with over 40 years of experience. He has led several research and development projects involving, for example, the analysis of uncertainties of dispersion models, the statistical evaluations of hazardous gas dispersion models, the development of models for the dispersion of emissions from tall power plant stacks, from offshore oil platforms, and from accidental and intentional releases of hazardous chemicals, and the analysis of data from large urban and regional field experiments. From 1988-1997, Dr. Hanna was Chief Editor of the *Journal of Applied Meteorology*, and has published over 150 articles in refereed journals, six chapters in books, and five books in which he is the primary author.

Dr. Ian Sykes

Dr. Sykes (BA, Cambridge in Math; Ph.D., Imperial College, London in Math) is Technical Manager of the Environmental Sciences Group of Sage Management. He joined the company in 2008 and has been involved in the numerical computation of environmental fluid dynamic phenomena associated with turbulent transport in the atmosphere. Prior to joining Sage, Dr. Sykes worked with Titan Corporation, then L-3 Communications. He has developed numerical models for the dispersion of material in buoyant jets ejected into a turbulent environment, and also to calculate the flow over three-dimensional terrain features. As a Principal Investigator, Dr. Sykes has played a key role in the development of a hierarchy of new dispersion models for EPRI (Electric Power Research Institute) and Defense Threat Reduction Agency (DTRA) which use advanced turbulence modeling techniques to describe both the dispersion and the statistical nature of the fluctuating concentration field.

Table 2: Summary of evaluation criteria for selected models

Model Category	Model Name	Freely available	Availability of Graphical User Interface	Complexity of Inputs	Validated against dense gas experiments	Able to represent a range of source configurations	Ability to account for complex terrain and obstructions	Ability to account for complex meteorology
Integral	SLAB	Yes	Purchase	Medium	Yes	Medium	None	Low
	DEGADIS	Yes	Purchase	Medium to High	Yes	Low	None	Low
	HGSYSTEM	Yes	No	Medium to High	Yes	High	Low	Low
	ALOHA	Yes	Free	Low	Yes	Low	None	Low
	EFFECTS (v10)	No	Purchase	Medium	Yes	High	None	Low
	SAFER/ TRACE	No	Purchase	Medium	Yes	High	None	Low
	GASTAR	No	Purchase	Medium	Yes	High	Medium	Medium
	PHAST	No	Purchase	Medium	Yes	High	None	Low
3D Eulerian	CHARM (flat terrain)	No	Purchase	Medium	Yes	High	None	Medium
	CHARM (complex terrain)	No	Purchase	Medium	No	High	High	Medium
Lagrangian puff and particle	SCIPUFF	Yes	Free	High	Yes	High	Medium	Medium
	MicroSPRAY ArRisk	No	Purchase	Medium	Yes	High	High	High
CFD	FLUENT, PANACHE, FLACS	No	Purchase	High	Yes	High	High	High
	OpenFOAM	Yes	No	High	Yes	High	High	High

Table 4A. Downwind distances for releases from a 2500 Ton ammonia ship.

No.	Type	Amount	Type of Release	Amount Released (Tons)	Wind Speed (m/s)	Wind Direction	Ambient Temp (°C)	AEGL-3 (10 min) Distance (m)	AEGL-3 (30 min) Distance (m)	LCT01 Distance (meters)	LCT90 Distance (meters)
1	2500 ton Ship	2 Tanks	Surface	1100 T (1)	1.5 Stab: F	To the SW	10	170	150	150	130
2	2500 ton Ship	2 Tanks	Surface	1100 T (1)	1.5 Stab: F	To the SE	10	160	160	160	140
3	2500 ton Ship	2 Tanks	Surface	1100 T (1)	3 Stab: D	To the SW	25	170	160	150	140
4	2500 ton Ship	2 Tanks	Surface	1100 T (1)	3 Stab: D	To the SE	25	160	150	140	110
5	2500 ton Ship	1 Tank	Surface	520 (1)	1.5 Stab: F	To the SW	10	150	140	100	70
6	2500 ton Ship	1 Tank	Surface	520 (1)	1.5 Stab: F	To the SE	10	120	120	110	90
7	2500 ton Ship	1 Tank	Surface	520 (1)	3 Stab: D	To the SW	25	120	120	110	95
8	2500 ton Ship	1 Tank	Surface	520 (1)	3 Stab: D	To the SE	25	110	110	100	90
9	2500 ton Ship	2 Tanks	Surface	1100 T (1)	10 Stab: D	To the SW	25	300	220	190	140
10	2500 ton Ship	2 Tanks	Surface	1100 T (1)	10 Stab: D	To the SW	25	280	215	140	125
11	2500 Ton Ship	2 Tanks	Surface	2500 T	10 Stab: D	To the SW	25	400	300	300	250

Figure 1: LCT curves, Scenario 1: 2 Tank 1100 metric ton release with a 1.5 m/s wind

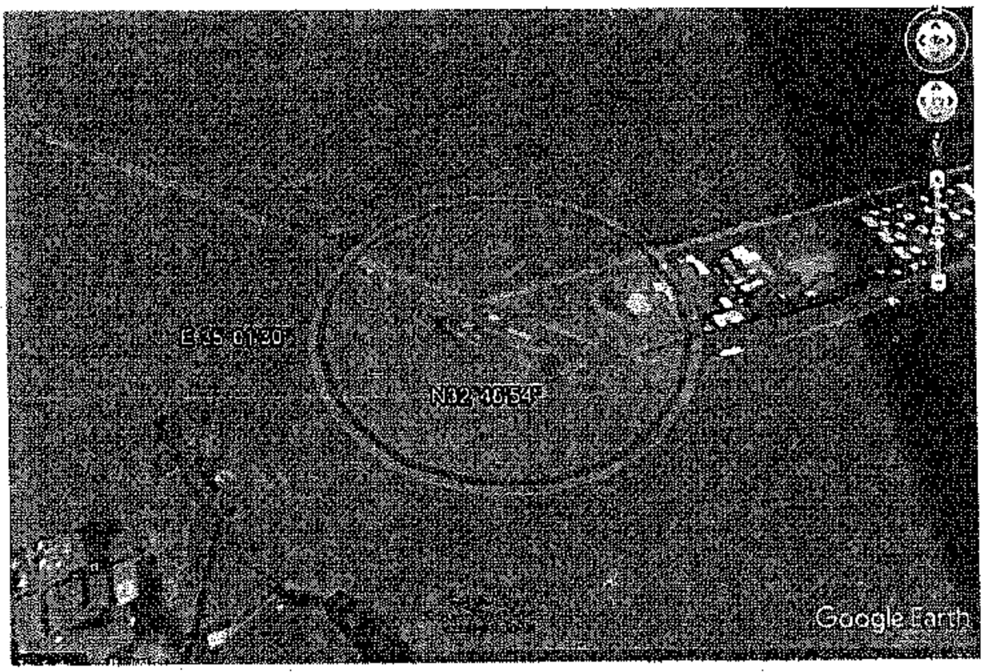


Figure 2: LCT Curves Scenario 10: 2 Tank 1100 metric ton release with a 10 m/s wind

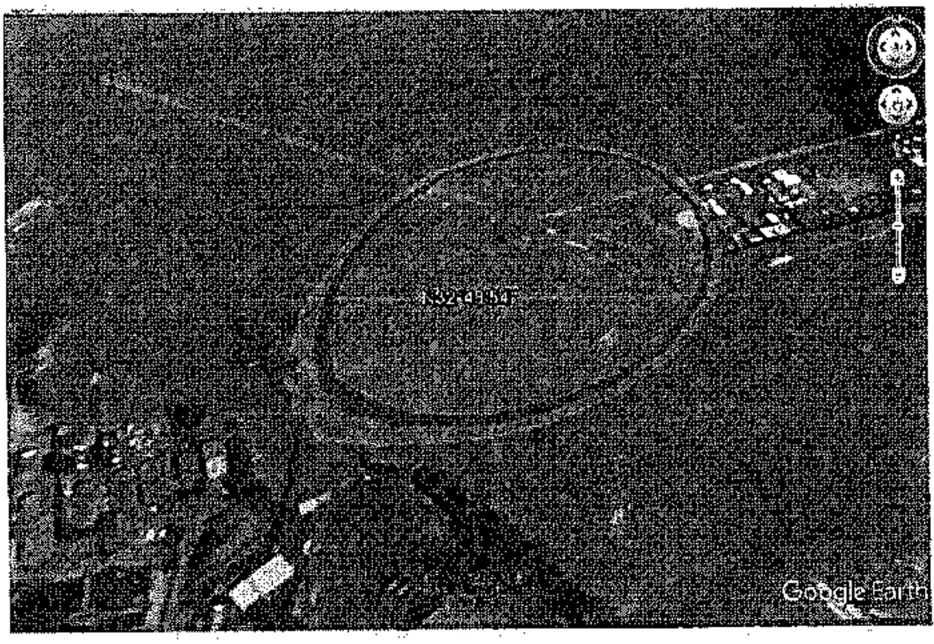


Figure 3: LCT Curves for Scenario 11: 2 Tank 2500 metric ton release with a 10 m/s wind

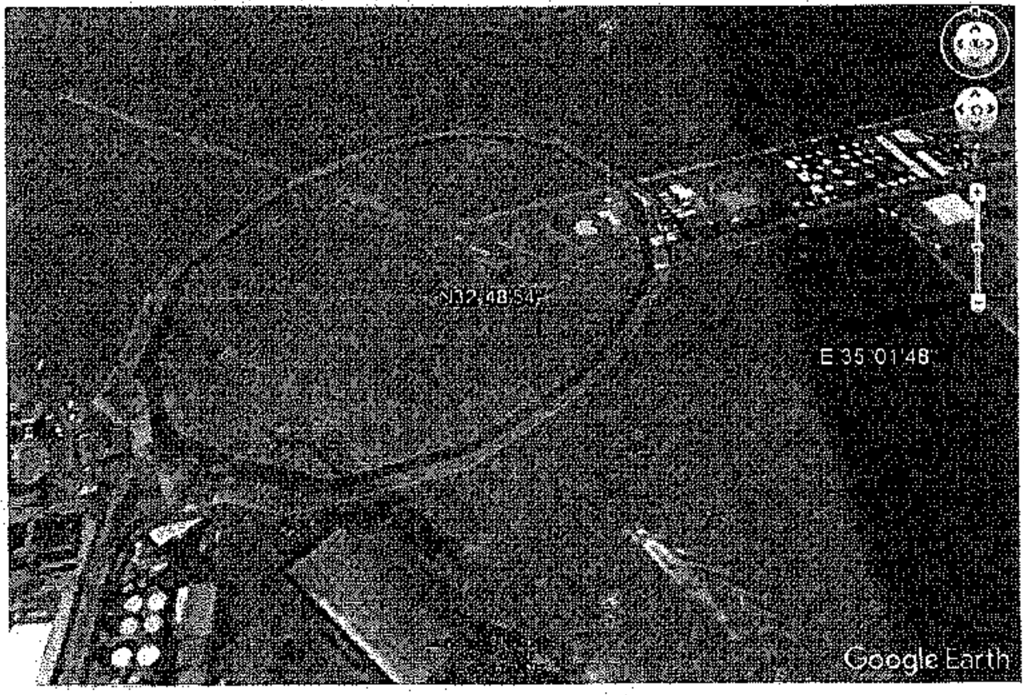
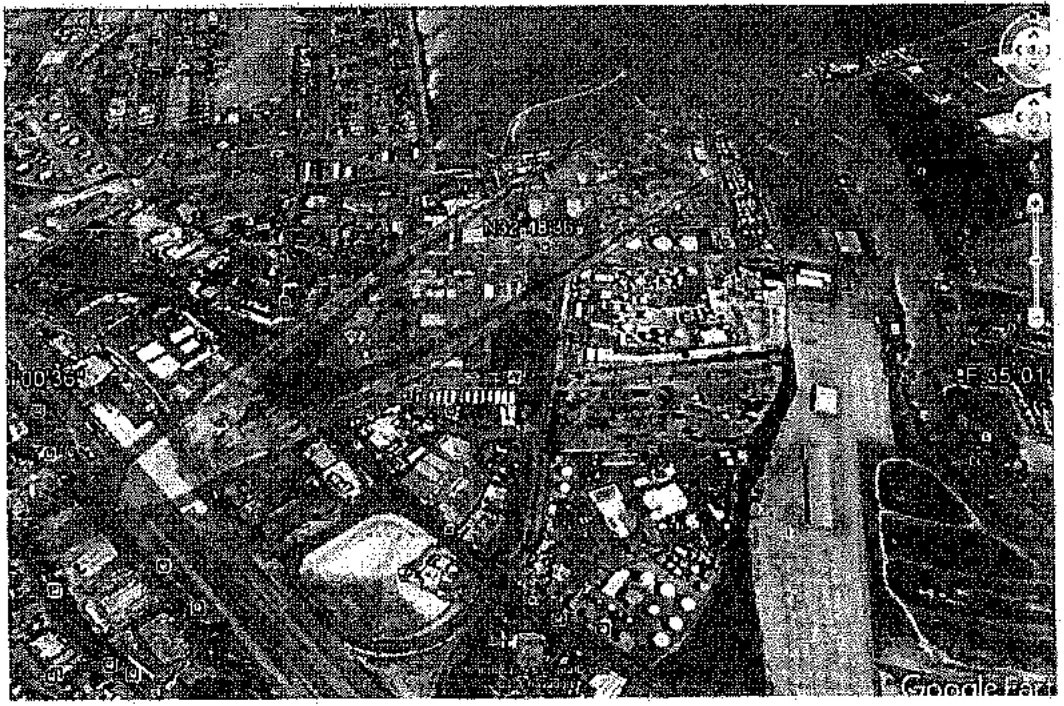


Figure 4; LCT Curve for Scenario 20; 2 Tank 2500 metric ton release with a 10 m/s wind; no buoyancy



APPENDIX

Description of Commonly Available Atmospheric Transport and Dispersion Models

Empirical correlations

This type of model seeks to relate several quantities by an empirical relation, assuming that the experimentally-derived relationship is applicable under other conditions. For example, these models provide a correlation between the centreline concentration and downwind distance for either instantaneous or continuous dense gas releases.

The empirical relations should be based on fundamental science principles (for example, dimensional analysis)

The best known example is the equations and nomograms in the 'Workbook on the dispersion of dense gases' (Britter and McQuaid 1988). Experimental data from many laboratory and field studies were plotted in dimensionless form, and are intended to provide guidance that incorporates the primary physical principles.

These correlations do not account for variables such as surface roughness length, averaging time or atmospheric stability conditions, and the effects of the initial source are assumed to be unimportant at the downwind distances of interest (Hanna et al. 1996). Nevertheless, in the (Hanna et al. 1993a) evaluation of several dense gas models with data from several field experiments, the Britter and McQuaid formulations provided just as good agreement with observations as the other more complicated models.

The Workbook correlations are regarded as a useful tool, and provide a convenient method to estimate the behaviour of dense gas clouds. The nomograms correlate well with the available large-scale experimental data, and are suitable for use within the range of data covered by the field observations. The Workbook correlations are only recommended for use as a benchmark screening model, and should not be applied to scenarios that are not very closely related to the original observations (Hanna et al. 1996).

Integral models

Integral models assume that the gas cloud has a dense central core, with Gaussian edges to the sides and vertically, and are based on the (Colenbrander 1980) and (te Riele 1977) formulations from 30 to 40 years ago. They use ordinary differential equations (as opposed to partial differential equations) to describe the bulk properties (or integral properties) of a dense gas cloud, including the radius of the gas plume, the plume's velocity, and centre line concentrations within the gas plume. Dense gas dispersion is typically modelled from a point just downstream of the source to a point where the density of the cloud becomes 'neutral'. After this point the cloud can be modelled using standard Gaussian atmospheric dispersion models. Integral models may have the capability to calculate release rates, but often the strength of the source and release rates over time must be calculated separately using a separate source term model.

The integral models considered herein are: HGSYSTEM, SLAB, DEGADIS, ALOHA, SAFER TRACE, GASTAR, PHAST and EFFECTS. HGSYSTEM contains HEGADAS, which was the first model based on te Riele (1977) and Colenbrander (1980). An overview of each model is provided below.

HGSYSTEM

HGSYSTEM is a suite of programs designed by Shell Research Ltd and select industry groups to assess the release of gases, liquids, and two-phase mixtures from a variety of sources and the subsequent dispersion of heavier-than-air and neutrally buoyant gases (Shell 1994). The suite of HGSYSTEM model components may be used separately or consecutively to describe a release from a source, near-field dispersion, and far-field dispersion (Fthenakis 1999). This system utilizes the HEGADAS program, which was the first integral model code developed for heavy gas dispersion, and is based on the suggestions of Colenbrander (1980), a scientist working in Shell's research group at the time. The code was originally developed to treat dispersion of LNG vapor evaporated from the surface of a spilled pool (i.e., an areas source). Further development of HEGADAS is described by (Witlox 1988). HGSYSTEM also includes models for initial two-phase jet releases and for instantaneous puff releases. Details on HGSYSTEM are available at www.hgsystem.com, where the code can be downloaded for free. The HGSYSTEM does not have an inbuilt Graphical User Interface (GUI) and must be run using a command prompt window and a text editor to modify the input files. The modular nature of HGSYSTEM, the versatility of the system, and the lack of a GUI increase model complexity, requiring more substantial training in the model.

Shell uses the Fire Release Explosion Dispersion (FRED) software that incorporates HGSYSTEM, and it used to be sold as a commercial package. However, since 2012 it is no longer commercially available.

SLAB

The SLAB model was developed by the Lawrence Livermore National Laboratory of the United States to simulate the atmospheric transport and dispersion of dense gases (Ermak 1990). The code for SLAB is freely available for download from the US EPA website (US-EPA 2012) and may be run using a DOS prompt window. The US EPA used SLAB to develop the tables in its RMP (Risk Management Plan) Guidelines. A GUI for SLAB, called SLAB View, can be purchased from Lakes Environmental (Environmental 2014). SLAB (with a GUI) is also available in the following commercial packages:

- BREEZE (Breeze 2014).
- EFFECTS (TNO 2014)
- CANARY (Johnson and Cornwell 2007) (Quest 2014)

SLAB is generally considered to contain excellent science, and is relatively easy to use, particularly with a GUI, though specific training in the model design and input-output parameters is required.

DEGADIS

The Dense Gas Dispersion (DEGADIS) model was originally developed for the United States Coast Guard and the Gas Research Institute to simulate the atmospheric dispersion of dense gases following LNG spills (Havens and Spicer 1988). Algorithms for simulating two-phase jet releases were added in the 1990s. The code for DEGADIS is freely available for download from the US EPA website (US-EPA 2012) and may be run in a DOS prompt window. A simplified version of DEGADIS is used as the dense gas model in ALOHA. DEGADIS (with a GUI) is also available as an option in the BREEZE Incident Analyst software package (Breeze 2014). DEGADIS is considered to be relatively difficult to use, particularly without a GUI. Substantial training in model design and input-output parameters is required.

ALOHA

ALOHA (Areal Locations of Hazardous Atmospheres) was developed by the United States Environmental Protection Agency and National Oceanic and Atmospheric Administration to simulate airborne releases of hazardous chemicals (Reynolds 1992). Most fire departments in the US have CAMEO/ALOHA. The United States National Safety Council distributes ALOHA and provides technical support. ALOHA can be used to model the release and dispersion of both neutrally buoyant and dense gases. Dense gas dispersion within ALOHA is based on the DEGADIS model, though the DEGADIS variant included within ALOHA has been simplified. ALOHA users may choose between several specified release options, including a gas leak from a ruptured pipe. Based on the selected scenario, the program will calculate the release rate as a function of time. The user may also specify a release rate using the direct source option (US-EPA 2007). ALOHA is freely available as part of the CAMEO (Computer-Aided Management of Emergency Systems) suite of software applications (US-EPA 2014). This suite includes a freely available GUI that is easy to use and is used by many fire departments and emergency responders in the United States. The model includes a database of chemical parameters for a number of chemicals, including CO_2 and default options for source emissions. The ALOHA GUI has been specifically designed for simplicity of use in the emergency response environment.

SAFER TRACE

The SAFER Systems TRACE (Toxic Release Analysis of Chemical Emissions) module is a dispersion modelling tool that can simulate a wide range of accidental toxic gas releases, including those associated with dense gas releases. The program is menu driven, and contains several separate modules to estimate the release and dispersion of chemicals. SAFER TRACE is a commercially-available set of consequence assessment tools and is available for purchase (Safer Systems 2014). SAFER TRACE is designed for speed and ease of use, though specific training in the model design and input-output parameters is required.

SAFER/TRACE is often purchased along with a comprehensive system that includes an on-site meteorological tower, on-site computers, and automatic communications to plant managers and emergency responders. It was once a fully-owned subsidiary of Dupont, who installed the system at many of their plants, but has been an independent company for the past 10 years.

TRACE scientists have contributed model outputs to several model intercomparison studies such as Hanna et al. (1993 and 2008), and are currently active members of the modelling group for the Jack Rabbit II chlorine field experiment.

GASTAR

GASTAR is a dense gas dispersion model developed by Cambridge Environmental Research Consultants (CERC 2009) in association with the HSE. Rex Britter was the primary developer of GASTAR and original author of the technical documentation. GASTAR can model dispersion of dense gases from a number of accident and emergency response scenarios. However, GASTAR is unable to calculate the source terms for all these scenarios, so they must be provided by the user.

GASTAR can be purchased from CERC (CERC 2014). The application has a Windows friendly GUI, simplifying input data entry and providing flexible examination of output. Although GASTAR is also supplied with a database of material properties for common toxic and flammable substances, CO_2 is not included in the database and the physical properties of CO_2 must be added by the user. GASTAR is designed to be as straightforward as possible, though specific training in the model design and input-output parameters is required.

PHAST

PHAST (Process Hazard Analysis Screening Tool) is a consequence analysis program for modelling accidental releases of hazardous materials (Witlox and Holt 2004). PHAST is available commercially from Det Norske Veritas - Germanischer Lloyd (DNV-GL) (DNV-GL 2014), a non-governmental organization that establishes and maintains technical standards, and supports this activity by undertaking in-house and sponsored research. The PHAST software is capable of assessing release rates from accidents and modelling subsequent dense gas dispersion. The PHAST GUI allows for a wide range of tabular and graphical output. PHAST is designed to be quick to setup and run and to require relatively limited training. PHAST has recently been enhanced to include results from CO_2 field experiments involving jets. The model has been widely evaluated against a comprehensive set of field observations and the results reported in the peer-reviewed literature.

EFFECTS

EFFECTS is a consequence analysis program for modelling hazards from accidental releases of hazardous materials. EFFECTS is available commercially from Netherlands Organisation for Applied Scientific Research (TNO 2014), which is an independent a non-profit organization. EFFECTS is capable of assessing release rates from accidents and modelling subsequent dense gas dispersion, with the methods and calculations published in the 'coloured books' (TNO 2005a, b, d, c). The GUI allows for a wide range of tabular and graphical output.

8.5.2 Lagrangian particle and plume dispersion models

Lagrangian particle and plume dispersion models have been developed to address the problem of characterising the dispersion of toxic gases in the presence of wind fields that are variable in time and space. The term Lagrangian in this case means 'following the flow field'. The transport and dispersion of either particles or puffs are simulated by Lagrangian models, and they can be applied to any type of terrain (flat, hilly, urban, forest canopy, etc.). For example, (Kaplan and Dinar 1996) describe a Lagrangian particle model applied to built-up urban areas, which are characterised by complex flow phenomena in the wake of buildings and flow channelling in the streets.

In general, Lagrangian modelling involves tracing the trajectories of fluid markers (particles or puffs) in a turbulent flow field, using a coordinate system that follows the fluid flow. The flow field is typically modelled by combining an initial wind field with a number of empirical correlations describing the turbulence structure. In urban applications, additional empirical correlations are provided for wakes formed on the upwind, lee-side and far-wake regions associated with buildings. The velocity and acceleration of a fluid particle are characterised in terms of the Lagrangian turbulent velocity and the Lagrangian time scale.(Kaplan and Dinar 1996).

Simulations using Lagrangian dispersion models can be run relatively quickly, making this a more preferable method than CFD for use in emergency response situations.

The Lagrangian models considered herein are: QUIC, SCIPUFF and MicroSPRAY. An overview of each model is provided below.

QUIC

The QUIC (Quick Urban & Industrial Complex) dispersion modelling system was developed at the Los Alamos National Laboratory (LANL) in the USA to predict the 3-

dimensional flow of pollutants around buildings and other obstacles. It is comprised of QUIC-URB, a model that computes a 3D mass-consistent wind field for flows around buildings, QUIC-PLUME, a model that describes dispersion near buildings, and a graphical user interface QUIC-GUI. The QUIC-PLUME model includes the ability to model the dispersion of heavier-than-air gases (Williams et al. 2005).

QUIC is currently available from LANL for non-profit research purposes only, but commercial licensing is currently under consideration. More than 200 research licences have been granted for QUIC, in applications ranging from urban micro-scale air quality, to dense gas dispersion for accidental releases, to homeland security applications (M. Brown, personal communication, 2014). Further details about QUIC are available from the LANL website[1]. As it is not commercially available, this model will not be considered in detail in this report.

SCIPUFF

The SCIPUFF (Second-order Closure Integrated Puff) transport and dispersion model uses a Gaussian puff methodology to provide a three-dimensional, time-dependent Lagrangian solution to the turbulent diffusion equations. SCIPUFF is an atmospheric dispersion model with a wide range of application. The turbulent diffusion parameterization is based on second-order turbulence closure theory, which relates the dispersion rate to velocity fluctuation statistics. In addition to the average concentration value, the closure model provides a prediction of the statistical variance in the concentration field resulting from the random fluctuations in the wind field. The variance is used to estimate a probability distribution for the predicted value. [17]

SCIPUFF uses a collection of Gaussian puffs to represent an arbitrary three-dimensional, time-dependent concentration field, and incorporates an efficient scheme for splitting and merging puffs. Wind shear effects are accurately modeled, and puffs are split when they grow too large for single point meteorology to be representative. These techniques allow the puff model to describe complex flow effects on dispersion, such as terrain-driven circulations.

SCIPUFF has been developed with a flexible interface, to describe many types of source geometry and material properties. The model also uses several types of meteorological input, including surface and upper air observations or three-

---

[1] www.lanl.gov/projects/quic

dimensional grid data. Planetary boundary layer turbulence is represented explicitly in terms of surface heat flux and shear stress using parameterized profile shapes. SCIPUFF is the primary AT&D tool in use by the US Department of Homeland Security (DHS) and Department of Defense (DOD). SCIPUFF calculations have been verified over the several years through live outdoor field trials including Prairie Grass conducted by DOD and Jack Rabbit I conducted by DHS.

CHARM

CHARM (Complex Hazardous Air Release Model) is a commercial Lagrangian puff model available from CharmModel.com. Two versions of CHARM are available:

The flat terrain version simulates a continuous release as a series of discrete puffs, which is a computationally quick approach, making this version of CHARM suitable for use in preliminary screening and emergency response scenarios.

The complex terrain version uses a 3D grid to perform the simulation, which is slower but useful for more detailed simulations.

CHARM operates in the Microsoft Windows environment, with an intuitive GUI and familiar menus and dialogue boxes. It is documented and comes with an on-line help system.

CHARM calculates the radiation footprint, overpressure footprint, or concentration of a chemical plume, and predicts the dispersion of the release. Simulation results are presented as tables as well as 2D and 3D graphics, including:

An instantaneous plume view showing the concentrations at a specified time since release.

A time-averaged plume based on a user-defined averaging interval.

A dose display showing the time history of concentration at any point.

A vertical cross-section of the plume.

A 3D view of a single user-defined concentration.

CHARM makes use of a 3D mass-consistent diagnostic wind model, similar to what is done in SCIPUFF, MSS, and QUIC.

3D Eulerian Grid / Computational Fluid Dynamics models

Three-Dimensional (3D) Eulerian grid models and CFD models use a set of advection-reaction-diffusion partial differential equations to describe the atmospheric dispersion of chemical species. The equations that are being solved include the Navier Stokes equations of motion, the equation of state, and several thermodynamic and chemical equations. Unlike Integral models, which use ordinary differential equations to describe the bulk properties of a dense gas cloud, the Eulerian approach is to calculate the specific cloud properties at each individual node of a 3D grid.

Numerical Weather Prediction (NWP) models used for weather forecasting can be considered Computational Fluid Dynamics (CFD) models, although their typical horizontal grid size is about 10 km. For dense gas applications, CFD models have horizontal grid sizes of 1 to 10 m.

The main advantage of CFD models applied to dense gas scenarios over the integral models and Lagrangian puff and particle models discussed above is that they allow for the explicit representation of complex terrain and space and time variable meteorological conditions and their effects on gas flow and dispersion.

The main disadvantage of CFD modelling is that it is generally substantially more expensive and time-consuming than the use of the integral models, though modern commercial CFD models are somewhat more user friendly and faster than historical systems. Use of CFD modelling requires significant specialised expertise.

While CFD models produce a more precise answer that is variable in time and space, it has not been demonstrated that they are any more accurate than simpler models when compared with field experiment observations.

FLUENT

FLUENT is a general-purpose CFD platform that can simulate the physics of dense gas releases and dispersion, as well as a wide variety of other physical phenomena.

Ammonia uses, accidents and consequences at large storage facilities*

Executive Summary

I have been asked to provide background on the general safety of handling ammonia, its historic safety record in the United States and other countries, and the identified safety features of the refrigerated ammonia storage tank in Haifa. My key conclusions are listed below:

1. Ammonia is one of the most widely used and transported chemicals in the world.
2. Ammonia's safety record in its 120 years as an industrial chemical is excellent.
3. In the last 22 years in the United States there have been a total of 2 ammonia inhalation fatalities resulting from an accidental release from a large ammonia storage tank.
4. In the last 22 years there has not been a single ammonia related fatality from a large ammonia tank incident outside the boundaries of the facility.
5. Most fatalities from ammonia exposure have occurred because of specific operational errors, or other causes, e.g. unrelated process explosions.
6. Ammonia stored under pressure in a container has far more significant consequences when it is breached than ammonia liquid in a tank that is refrigerated.
7. The ammonia tank in Haifa has unique safety features that ensure that an accidental or terror-related breach would have limited consequences.

Overview

Ammonia is a naturally occurring compound, and one of the most widely produced industrial chemicals in the world. It is a critical part of the natural nitrogen cycle. Each year 1-3 billion tons of ammonia is produced in natural processes, and over 140 million metric tons (MT) are produced synthetically for critical fertilizer and industrial uses, including food refrigeration and preservation[1]. Ammonia is transported billions of miles each year on roads, in pipelines, across waterways, and by rail. In the US, and other countries, ammonia is one of the most widely transported hazardous industrial chemicals[2]. The largest producers and users of ammonia are China, Russia, India and the United States. While ammonia is a hazardous substance that can be dangerous in high concentrations, its enormous importance in the global economy has caused industries and regulators around the world to enact safety protocols to ensure that risks of releases are minimized.

*M. Kent Anderson
President Emeritus, International Institute of Ammonia Refrigeration
Past Chair, Ammonia Safety and Training Institute