Understanding the Hazards and Potential Impacts of Ammonia Released to the Atmosphere

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Understanding Hazards and Consequences

- Typical transportation and storage conditions
- Discussion of potential hazards of ammonia loss of primary containment (LOPC)
  - Fire and explosion
  - Toxicity
- LOPC scenarios
- Modeling of identified scenarios and hazards
- Mitigating effects
- Conclusions

Transport and Storage Conditions for Ammonia

- Transport and storage conditions for ammonia in the liquid state
- Refrigerated ($T \leq NBP = 239.8\ K = -33.3\ ^\circ C$)
- Semi-refrigerated ($T \geq NBP$ and $P \geq 1\ atm$)
- Pressurized ($T = T_a$ = ambient temperature and $P \geq$ ammonia vapor pressure at T_a)

Potential Hazards

- Fire and explosion hazards
  - "Normal" hazards due to fire
  - Deflagration (flash fire): lower maximum side on overpressures and typically longer duration pressure waves (tens of ms), typical of the ignition of a vapor cloud (such as Flixborough accident)
  - Detonation: much higher maximum side on overpressures but typically short duration (tens of μs), typical of highly energetic materials (such as TNT)
  - Deflagrations can be accelerated into detonations under confined or congested conditions.
- Toxicity hazards
  - Frequently characterized using AEGLs

Fire and Explosion Consequences

- Consequence of fire or explosion depends on the total amount of energy released and how quickly that energy can be released.
- Total energy available is proportional to the amount of material involved (total mass) and the Heat of Combustion.

Material	Heat of Combustion (MJ/kg)
Ammonia	18.6
Ethanol	27.0
Hexane (stand in for gasoline)	44.9

Ammonia Fire Video

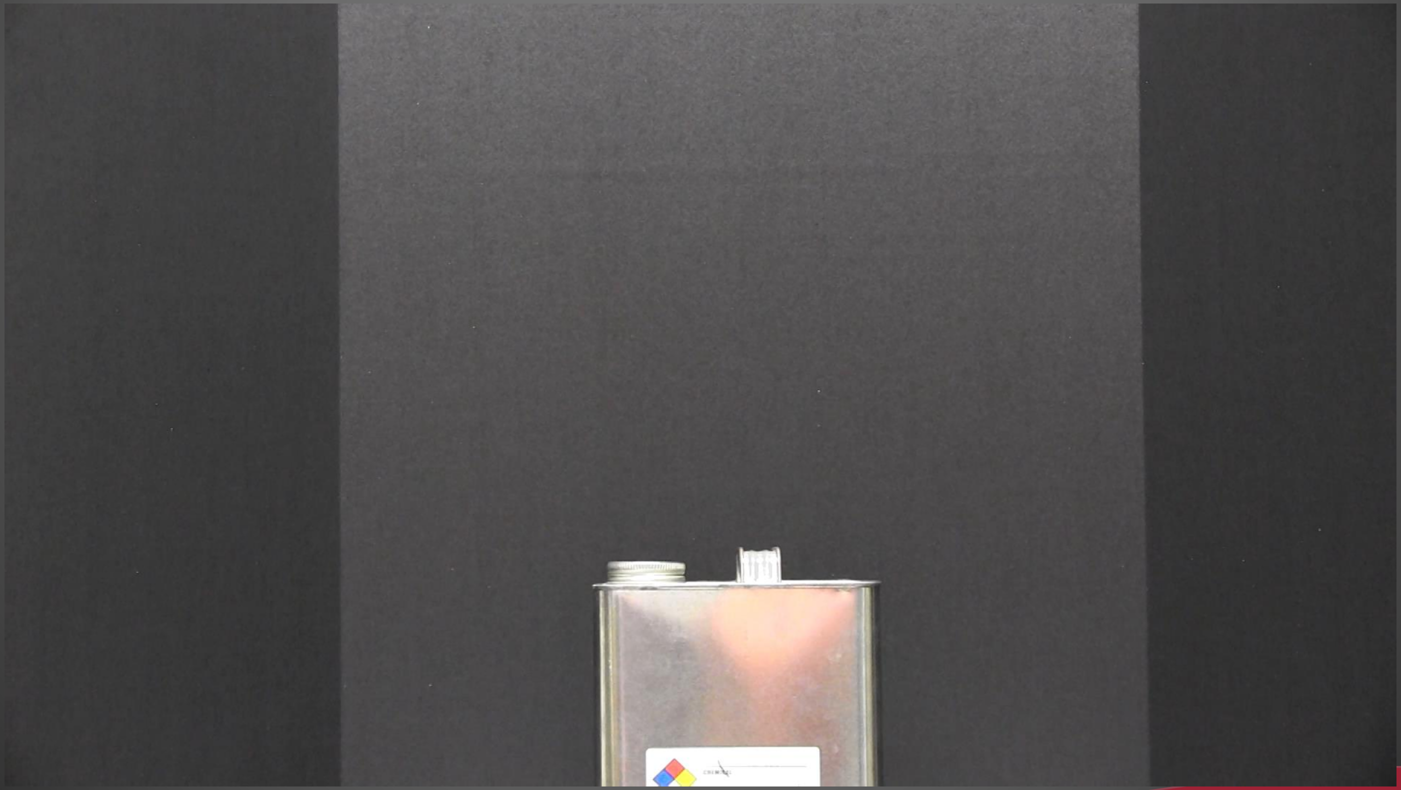
- Ammonia vapor premixed with air so that it is in the flammable region.
- As fire starts, burning ammonia/air is pushed out of the CONEX container initially.
- YouTube video: https://youtu.be/n4ktAaGAyLc

Gasoline Fire Video

- (Liquid) Gasoline in a standard container at room temperature. Vapor space contains air and gasoline vapor.
- Expect more energy to be released? Will it be released faster?

Ethanol Fire Video

- (Liquid) Ethanol in a standard container at room temperature. Vapor space contains air and ethanol vapor.
- Expect more energy to be released? Will it be released faster?



Fire Videos

- Hazards depend on the energy content as well as how quickly that energy can be released. In turn, this depends on the amount of air present to support combustion.
- How much air is needed?
  - Lower Flammable Limit (LFL) is where there is just sufficient fuel to burn in air
  - Upper Flammable Limit (UFL) is where there is just sufficient oxygen to burn in air

	LFL	UFL
Ammonia	15%	28%
Ethanol	1.2%	7.4%
Hexane (stand in for gasoline)	3.3%	19%

LFL and UFL Comparison

- Consider the volume of air per volume of chemical (V_a/V_c) representing LFL and UFL.

	LFL	LFL (V_a/V_c)	UFL	UFL (V_a/V_c)	Ratio of (V_a/V_c)
Ammonia	15%	5.7	28%	2.6	2.2
Ethanol	1.2%	82	7.4%	7.4	6.6
Hexane	3.3%	29	19%	4.3	6.7

- On this list, ammonia is the only material that is stored or transported as a pressurized liquid.
- For instantaneous releases of pressurized liquid, the violent nature of the release causes air to mix with the chemical. Estimates are that 10 times the volume of air is added per volume of chemical, so ammonia would be diluted below the LFL in an instantaneous release.

Fire and Explosion Consequences

- Conclusion: The impact of a fire strongly depends on how quickly the energy is released, and this depends on the amount of air present for many chemical fuels including ammonia.
- Conclusion: There is a limited range of the amount of air added to an ammonia cloud necessary for it to burn.
- Conclusion: For instantaneous ruptures of pressurized liquid ammonia, the amount of air expected to mix during the release would make the resulting cloud not flammable.

Fire and Explosion Consequences (2)

- What about explosions?
- Detonation has been observed in experiments using ammonia/oxygen mixtures when the entire mixture was within the flammable range.
- For an explosion to occur, a significant mass of an ammonia/air cloud would have to be within the narrow flammable limits for ammonia. This is not a practical concern for an accidental release.

Toxicity

AEGLs are the concentration (typically parts per million, ppm) of a substance above which it is predicted that the general population (including susceptible individuals) could experience:

- AEGL 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.
- AEGL 2: Irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
- AEGL 3: Life-threatening health effects or death.

Toxicity (2)

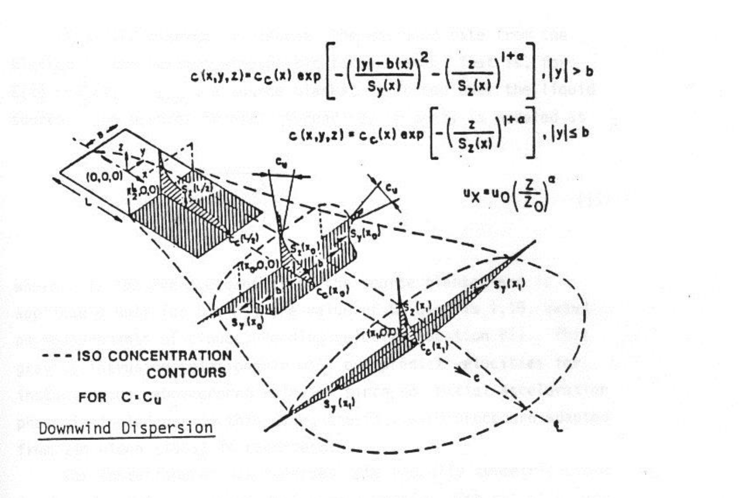
- Typically, AEGL 2 and 3 are based on a minimum probability (1%) of individual response from a population that includes susceptible individuals.
- In the case of ammonia, AEGL 3 is based on a probit equation using a causative variable of $C^2T = 7.3 \times 10^7$ where C is the (constant) concentration (ppm) of ammonia for exposure lasting T (min). This can be calculated as $\int C^2 dT$. (The AEGL 2 for ammonia is also based on a probit equation.)

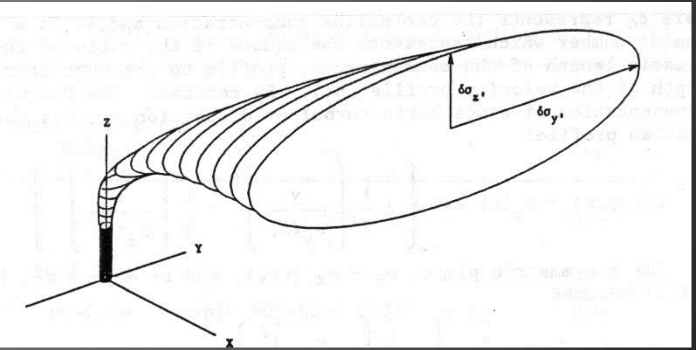
LOPC Scenarios

- Refrigerated liquid ammonia release onto water.
  - In small scale releases, around 70% of a liquid ammonia release was dissolved in water; only around 30% dispersed in air
  - In larger scale releases, around 50% of the liquid was dissolved in water, and 50% dispersed in air as a buoyant plume.
  - Model as a buoyant atmospheric plume. Consider toxic and flammable concentrations.
- Semi-refrigerated liquid/vapor ammonia release under water.
  - No significant ammonia vapor was dispersed in air in large scale releases under water at a depth of 0.9 m.
  - No further atmospheric dispersion modeling appropriate?
- Pressurized liquid release on land.
  - Consider instantaneous LOPC
  - Model as air/ammonia cloud. Consider toxic concentrations.

DEGADIS Modeling

- Developed for US Coast Guard and US Environmental Protection Agency to model denser-than-air contaminants from ground-level area (low velocity) sources and higher velocity vertical sources. (Some parts of DEGADIS were incorporated into ALOHA.)
- Verified against a wide variety of field scale release including the (pressurized ammonia) Desert Tortoise Tests.
- Predictions downwind of the horizontal jet release (800, 3,500, and 5,500 m) were in general agreement with observations.





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DEGADIS Desert Tortoise

	Maximum Concentration at 800 m (ppm)	Estimated σ_z at 800 m (m)	Estimated σ_y at 800 m (m)	Maximum Concentration at (ppm)	Maximum Concentration at (ppm)
DT1 Observed	11,200	3.8	31	670 @3.5 km	150 @5.5 km
DT1 DEGADIS	8,300	6.1	64	1040 @3.5 km	450 @5.5 km
DT2 Observed	18,600	4.8	74	4,000 @1.4 km	
DT2 DEGADIS	18,100	3.5	78	6,200 @1.4 km	
DT3 Observed	16,200	2.7	75	1,100 @2.8 km	
DT3 DEGADIS	13,700	4.8	69	2,050 @2.8 km	
DT4 Observed	21,000	3.1	101	5,100 @2.8 km	
DT4 DEGADIS	23,000	2.6	72	2,600 @2.8 km	

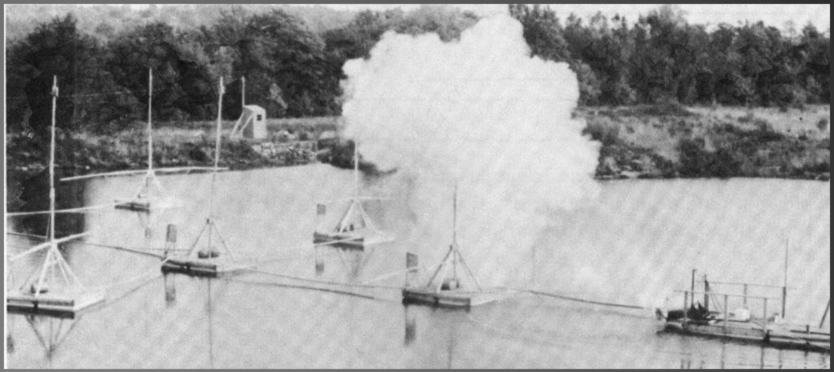
Example Scenarios

The following examples are meant to illustrate potential consequences.

Specifics of circumstances at Haifa have not been taken into account.

Refrigerated Liquid Release on Water Example

- Release rate before hitting water: 100 kg/s (comparable to DT)
- Buoyant gas release rate: 50 kg/s (DOT experiments)
- Estimate release area so that gas velocity is 2 m/s



Wind Speed	Atmospheric Stability	Maximum Distance to AEGL 3 / Elevation	Lowest Elevation to AEGL 3 / Downwind Distance
2 m/s	F	2000 m/240 m	25 m/6 m
10 m/s	D	1000 m/70 m	8 m/12 m

Pressurized Liquid Release on Land Example

- Mass released: 12.5 metric tons (instantaneously)
- Adiabatic flash fraction: 18.8%
- 10 times volume of air entrained at release
- Any reaction between ammonia and environmental surfaces are not taken into account.

Wind Speed	Atmospheric Stability	Maximum Distance to AEGL 3
2 m/s	F	1200 m
10 m/s	D	1000 m

Impact of External Energy Sources Example

- External energy sources (e.g., explosives or mortars) will increase the internal energy of the ammonia.
- Not all of the energy of an explosive will contribute to the internal energy of the ammonia.
- If an efficiency of 100% is used, a charge of 450 g TNT will vaporize 1.5 kg ammonia (raise the internal energy of the liquid so that it becomes a vapor).
- For the release examples considered here, there will be no significant difference in the impact.

Reaction with Environmental Surfaces

- Ammonia will react with environmental surfaces in a process typically modeled as dry deposition.
- Dry deposition velocities reported for ammonia are comparable to gases expected to undergo significant chemical reactions with environmental surfaces. These studies are all based on low concentration levels.
- When an ammonia cloud passes over water, the removal process will be enhanced because of the solubility of ammonia in water.

Conclusions

- The impact of a fire strongly depends on how quickly the energy is released, and this depends on the amount of air present for many chemical fuels including ammonia.
- There is a limited range of the amount of air added to an ammonia cloud necessary for it to burn.
- For instantaneous ruptures of pressurized liquid ammonia, the amount of air expected to mix during the release would make the resulting cloud not flammable.
- For an explosion to occur, a significant mass of an ammonia/air cloud would have to be within the narrow flammable limits for ammonia. Detonation has been observed in experiments using ammonia/oxygen mixtures when the entire mixture was within the flammable range.

Conclusions (2)

- A probit-based causative variable can be used to assess the consequences of time-varying releases for AEGL 3 exposures (also AEGL 2).
- Three basic loss of primary containment (LOPC) scenarios were considered
  - Refrigerated liquid ammonia release onto water. This scenario can be modeled as a buoyant plume with a significant amount of ammonia dissolved in the water at the spill site. Buoyant plume rise is very important in this scenario.
  - Semi-refrigerated liquid ammonia release under water. No significant ammonia vapor was dispersed in air in large scale experimental releases under water at a depth of 0.9 m.
  - Pressurized liquid release on land. This scenario can be modeled as an instantaneous release with initial rapid air mixing due to the violence of the release.

Conclusions (3)

- Smaller explosive charges will not significantly change the impact of any of the scenarios considered here. For larger explosive charges, the primary concern will likely be the explosive charge and not the effect on the ammonia being released.
- Ammonia reactivity with environmental surfaces will significantly mitigate the impact of a ground-level cloud, especially if the cloud travels over water.
- In assessing any release scenario involving a denser-than-air contaminant (pressurized storage scenario), it is important to recognize that the largest impact may not be at the lowest wind speed under the most stable atmospheric conditions.

Source Documents

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Questions?

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