R. Pitt

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Case Study of Fate and Effects of Ammonia Spills

Summary

Ammonia is one of the most common hazardous materials being transported in the U.S., especially in agricultural areas where it is used as an important fertilizer. It is also a common refrigerant and is frequently used in industrial areas. Ammonia is usually produced from natural gas, so it is also found in large quantities near petroleum producing areas. It is shipped throughout the country in ships and barges, rail tank cars, and tanker trucks.

Anhydrous ammonia (CAS No. 7664-41-7) is normally shipped in liquefied form (refrigerated on barges, pressurized on smaller carriers) and immediately vaporizes when lost (boiling point is -28^{o}F). Ammonia vapor forms a buoyant cloud. It has a high health hazard rating (3), but acute inhalation toxicity is much greater than uncomfortable odor level. It is highly irritating to throat at 400 ppm and eye irritation is noticeable at 70 ppm. The acceptable exposure limits are usually 25 to 50 ppm. It has a slight fire hazard rating (1) due to its narrow

explosive limits (16 to 25%). If it enters a receiving water, it is highly soluble and is toxic to fish (20 to 300 mg/L).

This module presents additional information for ammonia because of its common transportation, its high hazard ratings, and its unusual behavior when spilled. This module contains a description of the problems associated with spills of ammonia, and methods for predicting both air and water problems associated with ammonia spills. This example illustrates procedures for a toxic material for which specific methods have been developed (based on actual field studies). These procedures enable the calculation of the magnitude of potential exposures to these hazardous materials.

A case study for a recent ammonia spill associated with a train derailment in North Dakota is also presented to indicate the types of effects and problems a large ammonia spill may cause. In addition, a special report from New York describing ammonia accidents occurring from 1993 to 1998 is also attached to this module as a pdf file.

Case Study: Train Derailment and Spill of Anhydrous Ammonia, near Minot, North Dakota (Jan. 18, 2002)

The following links are to local news stories (*Bismarck Tribune*) on the day of the accident and a few days following:

http://www.bismarcktribune.com/articles/2002/01/18/189-brk-1.txt

http://www.bismarcktribune.com/articles/2002/01/18/191-brk-3.txt

http://www.bismarcktribune.com/articles/2002/01/19/140-nws-1.txt

http://www.bismarcktribune.com/articles/2002/01/19/141-nws-4c.txt

http://www.bismarcktribune.com/articles/2002/01/19/142-nws-3.txt

http://www.bismarcktribune.com/articles/2002/01/19/143-nws-2.txt

http://www.bismarcktribune.com/articles/2002/01/22/269-edt-1.txt

Link to a legal firm representing local residents in suit against CPRail, having many links to other related sources:

http://www.geocities.com/markwardt.geo/cprail.htm

Summary of Accident from Bismarck Tribune News Stories

A train derailment early Friday, January 18, 2002, sent a cloud of anhydrous ammonia over Minot, North Dakota, killed one man, sent part of a rail car slamming into a house and forced dozens of people to the hospital with breathing problems. The derailment, which happened about 1:40 a.m., knocked out power to about 1,000 people in parts of Minot and to Burlington, a small town just to the west. About 30 cars derailed, and 17 or 18 of the cars were carrying anhydrous ammonia, at least five were punctured. The train was headed from Medicine Hat, Alberta to Minneapolis, MN. The air temperatures were about 5^{o}F below zero. The cold temperatures and a lack of wind made the gas linger in the area. Previously, the town of Newburg, near Minot, was evacuated because of an ammonia leak in 1997.

More than 60 people went to the hospital and 13 were admitted, seven in intensive care. The Minot Fire Department sent a bus to evacuate the residents of Tierrecita Vallejo at about 7 a.m. Some were taken to the hospital, others to a triage center at Edison Elementary School, about five miles away. More than 80 people went to the elementary school. The following are quotes describing the experiences of some accident victims:

"'The entire house shook,' Jennifer Johnson said, still sobbing. 'I ran downstairs and looked out the window. I saw a giant white cloud coming right for me. Before I could look away it crashed through the window and burned my face. I couldn't see anything. I covered my face with a washcloth and went looking for my kids. We went down to the basement. The phone line was out, so I couldn't call 911. The only thing on the radio was music -- no one was telling us what happened or what to do. The kids were crying. We were burning up, our eyes were on fire. We were trapped.'"

"Johnson's other son Michael, 17, was trying to drive his Jeep out of the small community they lived in, just southwest of Minot proper. He heard an explosion. He saw a train car fly through a stand of trees and crash through Lee and Carmel Wieland's bedroom, a tail of fire following. The car missed the Wielands' bed -- and them -- by about a foot. It ripped through the side of the house, exposing the entire bedroom. The Wielands weren't touched."

"Down the street, a garage door hung sideways from the garage. The occupants of the house hadn't bothered to raise it in their haste to leave, and backed right through it."

The following comments were written in the aftermath of the accident:

"Many, many North Dakota communities are bisected by railroad tracks, carrying cars of anhydrous ammonia or worse. It's also common to meet farm vehicles pulling tanks of the deadly liquid fertilizer on the state's roads and highways."

"On trucks and rail, 'The biggest quantity coming through is mixed stuff, consumer commodities in cases,' said Battalion Chief Kurt Leben of Bismarck Fire and Inspections. After that is propane, then anhydrous, followed by diesel fuel, fuel oil and various solvents."

"'It could happen here' -- that's what went through peoples' minds as they learned about the Minot disaster. Not a groundless revelation at all. The Tribune, in response to the crash, asked local emergency officials if this community was prepared for an emergency like that in Minot. They said they were."

The following photos were published in the Minot Daily News:

Hazards of Accidental Releases of Ammonia during Transportation Operations

This discussion presents the results of a detailed site-specific evaluation of potential ammonia spills associated with transportation accidents. These accidents may range from complete loss of the cargo from specialized ammonia transport ships, losses during transfer operations, and losses during trucking of ammonia. Both water and air quality problems associated with these various spill conditions are addressed in this discussion. This discussion also considers a typical range of site meteorological conditions, not just worst-case conditions as described earlier (using the methods from the *Offsite Consequence Analysis* (EPA 1999) procedure).

Properties of Ammonia

Ammonia is a colorless gas at atmospheric pressure and normal temperature. It is alkaline and possesses a characteristic penetrating odor. On compression and cooling, ammonia gas condenses to a liquid about 60 percent as heavy as water. The liquid has a high vapor pressure at ordinary temperature, and commercial shipment requires pressure containers unless the liquid is refrigerated. Ammonia is readily absorbed in water to make ammonium hydroxide (NH_4OH). Considerable heat evolves during the solution of ammonia gas in water (1 lb NH_3 gas produces 937 Btu when dissolved in water).

Ammonia does not support ordinary combustion, but it does burn with a yellowish flame in an atmosphere of air or oxygen. The ignition temperature of ammonia-air mixtures is 780^oC, and the products of combustion are mainly nitrogen and water. Under certain conditions, mixtures of ammonia and air will explode when ignited. The explosive range for dry ammonia-air mixtures is about 16 to 25 percent ammonia. Admixtures with other combustible gases such as hydrogen, admixtures where oxygen replaces air, and/or higher than atmospheric temperatures and pressures will broaden the explosive range. Because this range is restrictive, the explosion hazard is usually ignored as being highly unlikely, and ammonia is generally treated as a nonflammable compressed gas. However, ammonia explosions have occurred associated with transportation accidents.

The major hazards associated with ammonia are from the toxic effects on breathing and caustic burns caused by vapor, liquid, or solutions. Also, the cryogenic properties of refrigerated liquid ammonia can present some unique hazards because of the extreme cold. The concentrations of ammonia vapor in the air that will cause various physiological responses in humans are given in Table 7-1. The toxic endpoint of ammonia, as defined in Appendix A to 40 CFR part 68, is 200 ppm (equivalent to 0.14 mg/L). This is the concentration used by EPA (1999) for offsite consequence analyses.

Table 7-1. Physiological Response to Various Concentrations of Ammonia (Kirk and Othmer)

Physiological Response	Approximate Ammonia Concentration in Air (ppm)
Least detectable odor	50
Maximum concentration allowable for prolonged exposure	100
Maximum concentration allowable for short exposure (1/2-1 hr)	300-500
Least amount causing immediate irritation to throat	400
Least amount causing immediate irritation to eyes	700
Compulsive coughing and possible death	1700
Dangerous for even short exposure (1/2 hr)	2500-4500

Potential Sources of Accidental Releases

Most leaks and spills of ammonia are caused by failure of equipment or mishandling by personnel. There are many sources for these releases. The most serious and probable of these sources are discussed below. The amounts of release are estimated for typical design conditions.

Vessels

1. A catastrophic accident, such as a collision involving a vessel could release a potential maximum of about 12,000 tons of liquid ammonia.

2. The refrigeration system on a vessel could develop a leak from a broken pipe or fitting. During a transfer operation, the loss during a 5-minute shutdown period could amount to about 125 lb, while without a transfer, the loss could be about 42 lb.

3. Spills could occur at a terminal during off-loading of a vessel. Because of automatic emergency equipment, the losses would be limited to line drainage between the automatic valves and the break. This loss could be about 7 tons.

Trucks and Rail Cars

1. Trucks and rail cars could be involved in accidents with subsequent leaks or spills. If there is a tank rupture, the entire ammonia cargo of up to about 20 tons/truck and 80 tons/rail car could be spilled almost instantaneously. A lesser amount could be lost through a tank crack or a broken fitting.

2. During the normal loading of a tank truck at a storage terminal, approximately 1 ounce of ammonia vapor may be released to the atmosphere through a vent stack usually 20 ft high.

Venting

Various pieces of equipment have relief valves that vent ammonia vapor if the pressure builds up to a prespecified level (usually caused by a rise in temperature from loss of refrigeration or from a fire.) This venting occurs in a controlled fashion as described below:

1. The relief valves on ammonia-carrying vessels can begin to vent after several days without refrigeration. These losses can amount to 200 to 500 lb/hr.

2. Large refrigerated storage tanks can vent after about 4 hours without refrigeration. The maximum vent rate can be about 750 lb/hr per tank. This would require an extremely long time to completely vent a tank. Backup electrical generators are typically used to supply electricity to the refrigeration equipment in case of prolonged power outages (the most probable cause of refrigeration failures).

3. The tanks on trucks and rail cars likely will vent only if involved in a fire. In a fire, a full truck tank would empty in about 4.5 hours, and a full rail car would empty in about 18 hours.

Water Quality Effects

The following discussion pertains to the hazards of spilling anhydrous ammonia during shipping and transfer operations at a facility located on a narrow ship channel. The discussion uses the ammonia (anhydrous)-specific, far-field prediction models provided in Raj, *et al*. (1974).

Anhydrous ammonia is a cryogenic liquid (boiling point is -28^{o}F) at normal atmospheric pressure. It floats on the water surface, rapidly dissolving within the water body into ammonium hydroxide (NH_4OH), while at the same time boiling into the atmosphere as gaseous ammonia (NH_3). The partition ratio (the quantity of ammonia that dissolves into the receiving water divided by the total quantity spilled) is normally between 0.5 and 0.8 for surface spills and somewhat higher for underwater spills. For simplicity, the partition ratio for these analyses is assumed to be 0.6 for all spills. Furthermore, all spills are considered to be instantaneous.

If the water body near the site is of a generally one-dimensional nature and lacks advective currents, the spill would be distributed evenly over the cross section of the channel. Furthermore, it is expected that the length of channel affected by the spill would be roughly proportional to the length of time elapsed after the spill. If one further assumes that the concentration is constant longitudinally behind the advancing pollution front, then a single concentration value can be calculated to represent the entire contaminated prism as a function of increasing channel length for a given spill quantity. These functions are plotted on Figure 7-1, which assumes a constant cross-sectional area of 10,000 ft^2 within a ship channel and a speed of the pollution-front advance of approximately 0.2 ft/sec (if the actual cross-sectional area is larger than 10,000 ft^2, the resulting concentrations would be correspondingly smaller; if the actual water velocities were greater than 0.2 ft/sec, the times for the indicated concentrations to reach a specific point would be correspondingly sooner).

In reality, a well-mixed pollutant diffuses along a one-dimensional channel. It is not concentrated evenly along the polluted channel length. The actual concentrations are inversely proportion to the distance from the spill point. It can be assumed that the single concentration values obtained for a given spill value and channel length (Figure 7-1) best represent those concentration values expected to be measured approximately midway between the spill point and the limit of the channel length affected. The actual values will be greater by a factor of between 1 and 2 than those shown near the spill point, and will be less than the plotted concentrations down-channel from the midpoint.

The downstream length before complete mixing across the channel occurs can be estimated using an equation presented by Thomann and Mueller (1987):

$$L_m = \frac{2.6UB^2}{H} \qquad \text{Equation 7-1}$$

where: U is the stream velocity in ft/second

B is the average stream width in feet, and

H is average stream depth in feet

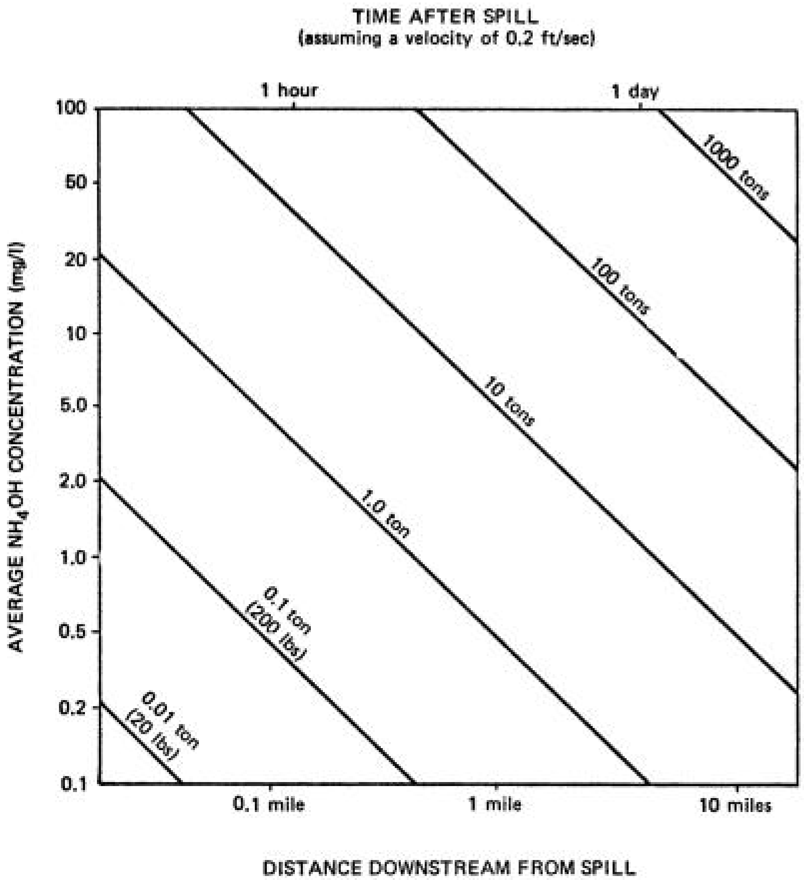

Figure 7-1. Mean ammonium hydroxide concentrations in estuarine prisms for various ammonia spill quantities.

For illustration, consider the following conditions approximating the above example:

U = 0.2 ft/sec

B = 285 ft

H = 35 ft

In this case, the "complete mixing" length would be about 1200 feet (0.22 mile). About half of this distance would be needed if the discharge location is located at the centerline of the channel. These are relatively short lengths for most of the spills represented in Figure 7-1, and would occur between one and two hours after the ammonia is released.

Air Quality Effects

The physical processes governing atmospheric dispersion when large quantities (over 1,000 tons) of liquid ammonia (LNH_3) are spilled instantaneously on, or under, water are not well understood. However, laboratory, swimming pool, and lake tests provide some insight into the dispersion behavior. These results offer tentative models for estimating potential atmospheric concentrations from spills.

The important parameters needed for analysis of instantaneous ammonia spills are the following:

- The amount of LNH_3 released;

- The actual ratio of LNH_3 that evaporates into the atmosphere when the accident happens on or under the water (one minus the partition ratio); and
- The estimated rate of rise of the NH_3 vapor cloud.

The partition ratio of 0.6 (from estimates developed by Raj, *et al.* 1974) has been applied in estimating ambient concentrations from spills. Raj and his associates also developed a plume rise model that seemed to agree well with observed cloud center heights and was considered conservative. During the same studies, well-defined Gaussian distributions of concentrations in the horizontal direction were observed. Therefore, Gaussian dispersion models (presented by Turner 1970), using Pasquill-Gifford stability classes, are applied in the following discussion for estimating the air quality impacts of hypothesized spills on both land and water.

Tank Ruptures on Vessels

Expected ambient concentrations were calculated for distances of 0.2 to 10 miles downwind from a hypothetical vessel accident in which an entire cargo of liquid ammonia (12,000 tons) was spilled into the water instantaneously. It was assumed that (1) the entire spill would spread over a circular area with a radius of about 800 ft and (2) 40 percent of the LNH_3 would evaporate in several minutes (based on projections from Raj, *et al*. 1974).

Since the density of NH_3 is only 60% of the density of air at the same temperature and pressure, atmospheric stability will have very little effect on the rate of rise of the NH_3. Because the rate of rise of the NH_3 is not controlled by atmospheric stability, the only way any part of the plume can reach the ground at a point downwind is through turbulent atmospheric transport. Stability classes A, B, and C are the unstable atmospheric classes, and by definition atmospheric instability fosters turbulent action. Stability class D is called the neutral class, but it embraces both stable and unstable conditions. For such a fast-rising gas (NH_3), it seems doubtful that the plume can return to the ground, even with unstable conditions. Since stable classes E and F have low levels of turbulence, calculations were made only for classes A, B, C, and D. Even with these unstable conditions, applying the Pasquill-Gifford equation is considered to be a conservative practice, yielding an overestimation of expected ambient concentrations. However, fumigation conditions during extreme inversions and shallow mixing heights would likely cause a worst-case condition.

Downwind distances to points at which selected concentrations were calculated to occur are summarized in Table 7-2. It should be noted that 0.2 mile is just outside the assumed spill area. It was assumed that concentrations within the spill area would be at least 5000 ppm (and quickly lethal).

The maximum durations of exposure for the various concentrations will be along the dispersion centerline in the horizontal plane at the ground and in the direct downwind direction. Away from this centerline, durations of similar concentrations will be shorter. These estimated, downwind duration values are summarized in Table 7-3. The durations are calculated for an instantaneous spill and will increase if the ammonia vapor is released over a longer period; however, concentrations will be correspondingly lower.

Table 7-2. Estimated Downwind Distances of Four Concentrations of NH_3 - Total Vessel Spill Of 12,000 Tons

Atmospheric Stability Class	Wind Speed (mph)	Downwind Distances (miles) for:			
		50 ppm	300 ppm	1700 ppm	5000 ppm
A	5	2.0	0.7	<0.2	<0.2
B	11	4.4	1.9	0.8	0.4
C	15	1.2	0.9	0.6	0.4
	25	9.0	3.5	1.6	1.0
D	£15	<0.2	<0.2	<0.2	<0.2
	25	0.6	0.5	0.4	0.3
	35	1.1	0.9	0.7	0.5
	45	2.0	1.5	1.1	0.8

Table 7-3. Estimated Durations Of Various Concentrations at Several Distances Directly Downwind of an Instantaneous Total Vessel Spill

Atmospheric Stability Class	Wind Speed (mph)	Estimated Duration (minutes) for:			
		^{3}50 ppm	^{3}300 ppm	^{3}1700 ppm	^{3}5000 ppm
At a distance of 0.5 mile					
A	5	19	8	0	0
B	11	9	7	4	0
C	15	4	3	1	0
	25	3	3	2	1
D	£15	0	0	0	0
	25	<1	0	0	0
	35	1	1	<1	<0.5
	45	1	1	<1	<0.5
At a distance of 1.0 mile					
A	5	18	0	0	0
B	11	9	6	0	0
C	15	3	0	0	0
	25	3	3	1	0
D	£15	0	0	0	0
	25	0	0	0	0
	35	<1	0	0	0
	45	1	<1	<1/2	0
At a distance of 5.0 miles					
A	5	0	0	0	0
B	11	5	0	0	0
C	15	0	0	0	0
	25	4	0	0	0
D	£15	0	0	0	0
	25	0	0	0	0
	35	0	0	0	0
	45	0	0	0	0

The values in Tables 7-2 and 7-3 indicate that:

- For atmospheric stability classes A and B, which involve only low wind speeds, ambient concentrations at a given distance are relatively low, but exposure durations are longer.
- For stability classes C and D, which generally involve higher wind speeds, ambient concentrations at a given distance are relatively high, but exposure durations are relatively short.

The ammonia cloud is not expected to touch the ground surface within 10 miles for stability classes E and F, because of the small dispersion coefficients and rapid rise of the NH_3 cloud. For all atmospheric stability classes, under certain terrain conditions, ambient concentrations higher than those calculated may occur, depending upon relative altitude and distance from the spill. As an example, a rising plume may strike the ground in an area of extreme topography or if high buildings are nearby.

In fog or low cloud conditions, some spilled NH_3 would react with the water vapor, becoming NH_4OH. This reaction would cause lower ambient concentrations and longer durations than those shown in Tables 7-2 and 7-3. In fog or a low stratus cloud layer, the lateral spread is expected to be small. In cumulus clouds, there would be greater lateral and vertical spreading. Since an NH_4OH molecule is about twice as heavy as a water molecule, it is expected that fallout would occur, primarily near the scene of the accident.

Other Malfunctions

Transfer Sills

Transfer spills could occur during the loading or off-loading of a vessel, truck or rail car. When modeling a potential spill in this category, it is assumed that the LNH_3 from a transfer spill would spread evenly on the land and completely evaporate in one hour or, for a spill duration of greater than one hour, for the duration of the spill. It also would be assumed that none of the ammonia would run off into the water. The spill would then act as a continuous source, allowing use of the Gaussian dispersion model for a continuous point ground-level source to predict concentrations downwind. Other malfunctions, such as venting from relief valves on vessels, storage tanks, trucks, and rail cars, can be described by the same model, with the only variation being the rate of venting or evaporation.

The highest concentrations would be estimated for stability class D, as discussed previously. For planning purposes, the calculations should be based on a wind speed of 10 mph because this value represents the most turbulent conditions expected to occur in class D.

Venting Leaks

With loss of refrigeration, LNH_3 will begin to boil (vaporize). As heat is absorbed from the surroundings, the temperature and pressure inside the tank will rise. Because of the heavy insulation of large LNH_3 storage tanks, about 4 hours without refrigeration can elapse before the relief valves begin to vent. Even higher pressure settings on relief valves on vessels means that several days without refrigeration would be required before the internal pressure would build to the point where venting begins. Maximum venting rates are expected to be about 200 to 500 lb/hr for vessel tanks.

Trucks and trains are designed to transport liquid ammonia under pressure at ambient temperatures. A fire in or near a truck or rail car could cause relief valves to open. The rate capacity of the relief valves is about 4.5 tons/hr of NH_3. The heat from a fire, in addition to causing the ammonia to boil, would create a strong updraft which likely would cause the ammonia vapors to quickly rise. A fire could also incinerate some of the ammonia vapors. Both of these conditions would combine to reduce ground-level concentrations to below those predicted here.

Tank Ruptures

Trucks and trains are susceptible to accidents which could create more serious hazard conditions than venting. The worst accident situation would be one in which the tank ruptured and instantaneously spilled 20 tons of LNH_3 (truck) or 80 tons of LNH_3 (rail car) onto the ground without a fire. Without the additional heat from a fire, no special supporting updraft would be created, and the ammonia cloud, though rising, would stay closer to the ground for a greater distance downwind, especially if foggy or rainy, or under strong inversion conditions. It typically is assumed that the entire cargo would spread out to a uniform depth of about 3 inches (EPA 1999 assumes a pool depth of 1 cm and the corresponding pool would therefore be about 7.5 times larger. The total evaporation rate would be similarly larger, but for a shorter duration). Ammonia pools of 3 inches in depth are expected to evaporate in approximately 2 hours. The evaporation rate would be 40 ton/hr (rail car) and 10 tons/hr (truck). If the LNH_3 is contained in a smaller area, if a smaller total amount spills, or if the atmosphere is in a condition other than class D and/or has higher wind speeds, ammonia concentrations downwind are expected to be less. Similarly, if the pool was 1 cm deep (as assumed by the EPA 1999 method), the ammonia would evaporate in about 15 minutes. The evaporation rate would be about 300 ton/hr (rail car) and 75 tons/hr (truck), and the corresponding downwind concentrations would be about 7.5 times larger than if a 3 inch pool was formed.

Summary of Effects on the Living Environment

Table 7-4 summarizes expected downwind distances and durations of ammonia concentrations for different spill conditions. The following discussion summarizes the expected impacts on living organisms associated with these spills.

Table 7-4. Estimated Downwind Distances of Concentrations of NH_3 for Various Transportation Accidents

Malfunction	Assumed Evaporation Rate (lb/hr)	Maximum Downwind Distance[a] (miles) for:				
		50 ppm	300 ppm	1700 ppm	5000 ppm	Assumed Duration
Vessel venting on loss of refrigeration	500	0.05	0.05	<0.01	<0.01	Until refrigeration is re-established and the NH_3 is cooled sufficiently
Truck or rail car transfer line accident	8,000	0.33	0.10	0.03	0.02	1 hr[b]
Truck or rail car venting in a fire	9,000	0.36	0.11	0.04	0.02	1 hr[b]
Vessel transfer line accident	14,000	0.48	0.15	0.05	0.02	1 hr[b]
Truck tank rupture	20,000	0.60	0.19	0.06	0.03	2 hr[b]
Rail car tank rupture	80,000	1.40	0.46	0.15	0.12	2 hr[b]

[a] Assumed wind speed, 10 mph; stability class D.

[b] If the durations are shorter (pool depths shallower) the concentrations will be greater; similarly, if the durations are longer, the concentrations will be less.

Human Population

Human physiological responses to various concentrations of ammonia were presented in Table 7-1. Depending on specific atmospheric conditions, it can be expected that people several miles downwind likely will have to be treated for ammonia inhalation effects for a vessel disaster. However, no deaths are likely to occur, except possibly very close to a loss site. Durations of exposure will increase if the ammonia vapor is released over a longer period of time (not instantaneously), but the concentrations at any given location will be correspondingly lower. The other types of accidents could generate downwind concentrations sufficient to cause noticeable odors up to 1.5 miles away. Evacuation might be required for up to 0.5 miles downwind, depending upon the type of accident. Because of ammonia’s characteristic odor at relatively low concentrations, people will likely respond by leaving an affected area before official warnings are issued. In some cases, however, it may be best if local residents remained in their homes and attempted to seal door thresholds with wet material instead of going outside and exposing themselves to higher concentrations. Communication with the local residents is therefore necessary.

Marine and Aquatic Organisms

In the event of a spill during the loading or off-loading of a vessel, ammonia could be leaked directly into the water. Assuming a line draining directly into the water, 7 tons of liquid ammonia could be lost. With a partition ratio of 0.6, 4 tons of NH_3 would go into solution as ammonium hydroxide, while the remainder would vaporize into the air. The toxicity of an ammonia solution in water is directly proportional to the concentration of nonionized NH_3 present. The amount of nonionized NH_3 is dependent on pH, temperature, and salinity. With a pH of 8.0, a temperature of 15^{o}C, and zero salinity, the percentage of nonionized NH_3 would be 5.7 percent. At a pH of 9.0, nonionized NH_3 would be 37.7 percent of the total ammonia concentration. This information then can be used to calculate the concentration of nonionized NH_3 in the water, as shown in the example below. A concentration of nonionized NH_3 greater than 1.25 ppm can be toxic to some freshwater fish.

With the pH range described above, assuming complete mixing within a channel having a 10,000 ft^2 cross-section, a 7-ton spill would produce toxic conditions for fish for a distance of about 1 mile along the channel. There would be a severe fish kill in the immediate vicinity of the spill where the concentrations of NH_3 would be highest. It can also be assumed that planktonic and benthic organism mortality would also occur in the vicinity of the spill.

A spill of lesser magnitude could occur if the refrigeration equipment on a vessel were to develop a leak from a broken pipe or fitting. Such a leak could release from 42 to 125 1b of NH_3 in 5 minutes. The effect of such a release probably would be confined to the local area. However, the possibility of a fish kill within the immediate area is likely.

In the unlikely event that a catastrophic accident were to occur causing the release of an entire vessel's contents, approximately 12,000 tons of NH_3 could be released into the water. Such a spill could ultimately cause toxic concentrations of NH_3 throughout a large area. The size of the affected area would change as the contaminated water moves downstream. There would be massive mortalities of fish, plankton, shellfish, and other benthic organisms.

A long-term result of any ammonia spill would be increased eutrophication of the receiving waters, depending on the presence of other needed nutrients. The additional nutrient levels could stimulate noxious blooms of algae, which would cause continuous water quality degradation.

Terrestrial Biology

In sufficiently high concentrations, ammonia is toxic to living organisms (Miner 1969, and Levine 1968). Large amounts of this chemical would be released into the environment in the event of a large leak or spill, such as a total vessel spill. Regardless of where a vessel ruptured along an inland route, high concentrations of ammonium hydroxide would likely reach shore. If this chemical floated into any of the wetlands bordering the shipping route, much of the vegetation would be killed, potentially causing destruction of important habitat for waterfowl, shorebirds, and other shore species.

Waterfowl and shorebirds present in the wetlands at the time the ammonium hydroxide came into shore could be directly affected. A large number of birds could be killed by ingestion of the chemical. The ammonium hydroxide could also strip protective oils from the feathers of waterfowl, causing the loss of the birds' natural water repellency. In this case, birds would die either from drowning or from infections contracted as a result of getting wet.

The ammonia which would escape into the atmosphere would form a plume with a concentration of several thousand ppm at its center. Concentrations of 1700 ppm or more of ammonia would occur for several minutes at sea level for a distance of several miles downwind from the location of a vessel accident or for longer periods but over a smaller area if the ship leaked slowly. It is likely that any bird or animal exposed to these high concentrations of ammonia would be injured or rapidly killed. Birds in the vicinity of the accident could possibly become disoriented in their attempts to escape the odor and might fly into the lethal part of the plume. If the vessel broke up near shore, animal and birds could be killed for several miles inland.

Severe damage to vegetation would also be expected to occur. The extent of this damage would depend upon the resistance of individual plant species to ammonia and the time of year the spill occurred. Plant species differ in their sensitivity to ammonia (Miner 1969). It is possible that some species may be able to withstand high concentrations of the gas for several minutes. In the spring or summer, a concentrated ammonia plume would probably severely damage most vegetation that it contacts. Perennial species in the natural flora would be most affected by ammonia in the summer and early fall when they are under the greatest physiological stress because of low soil moisture. Since seeds are most resistant to ammonia, annual species in the natural flora would not be greatly affected during summer months. These species would be hardest hit in the spring or fall.

Links to Associated Sources of Information

Canadian Center for Occupational Health and Safety

http://www.ccohs.ca/

U.S. Occupational Safety and Health Administration

http://www.osha.gov

Typical MSDS documents for ammonia and ammonia compounds:

Anhydrous ammonia:

http://www.fertilizerworks.com/html/msds_anhyd.html

Ammonium hydroxide:

http://www.cleartech.ca/msdss/AQUA.HTM

Strong ammonia solution:

http://www.adsrepro.com/html/ammonia_msds.html

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