

# Predicting Hazards from Ammonia Spills

Experimental and analytical results of studies of phenomena that occur when anhydrous liquid ammonia is released on or under the surface of water.

P.K. Raj, J.H. Hagopian, and A.S. Kalelkar  
Arthur D. Little, Inc.  
Cambridge, Mass.

J. Cece  
U.S. Coast Guard  
Washington, D.C.

A successful mathematical model technique has been developed that permits the prediction of the vapor hazard extent when a massive release of liquid anhydrous ammonia ( $\text{LNH}_3$ ) occurs on water.

Maritime transport of  $\text{LNH}_3$  on U.S. waters has increased rapidly. Ammonia is carried in barges as a high-pressure cargo in heavy-wall steel tanks, as well as a low-temperature cargo in atmospherically-pressured refrigerated tanks. There has been very rapid growth in refrigerated transport, motivated by the savings in capital costs associated with onshore refrigerated storage compared to pressure storage. The United States Coast Guard, recognizing the potential hazards from a spill on inland waterways, determined to evaluate these hazards and initiated a research program to study the aspects of spills on and under water. The main objectives of the study were to conduct experiments and develop theoretical models to predict the hazards that would be effected by spills of up to 3,000 ton of  $\text{LNH}_3$ .

The reaction of  $\text{LNH}_3$  and water is exothermic and results in the liberation of cold ammonia vapor (boiling point  $-28^\circ\text{F}$  at 1 atm.) and the formation of ammonium hydroxide. The relative amount of both forms depends largely on the manner in which the  $\text{LNH}_3$  and water are combined. Figure 1 shows a number of the possible ammonia-air-water interactions which may result from a spill on water.

Ammonia vapor's major hazard to human beings is its toxicity. Exposure to 5,000 ppm. in air may be instantaneously fatal. As with other toxic gases, longer exposures to correspondingly lower concentrations may have an equivalent effect. (1)

Ammonia is not highly combustible. Though its flammability limits in dry air are 15 to 28 vol.-%, its ignition temperature is relatively high. Tests by Husa and Buckley (2) in which  $\text{LNH}_3$  was poured into a pan showed that flashes of flame occurred when an ignition source was brought near the liquid surface, but that flames would not sustain themselves.

There have been no similar experiments with ammonia on water. If  $\text{LNH}_3$  burns on water, existing correlations (3)

show the flame height should be lower than for organic liquid fuel fires. Furthermore, ammonia fires should not be luminous, because of the absence of carbon. With less height and non-luminosity, it follows that ammonia fires should not radiate as much heat as organic fuel fires.

Accumulation of a flammable concentration of vapor in an enclosure and its subsequent ignition may lead to an explosion. Its force would depend on the degree of confinement. Buckley and Husa (4) found that pressure ratios observed in ammonia explosions are roughly three-quarters that found for hydrocarbon fuels. Attempts by these authors to detonate ammonia-air mixtures at atmospheric pressures failed.

The effects of large quantities of ammonia dissolving in water include a rise in the temperature and pH level of the water and the formation of ammonium hydroxide. Each of these may cause severe harm to aquatic life in the vicinity of a spill. Prolonged exposure to concentrations of a few ppm. can cause fish to suffocate. (5)

## One major land spill investigated earlier

There have been no experiments to date involving spills of  $\text{LNH}_3$  on water. However, a major land spill investigation was reported by Resplandy. (6) In these experiments, pressurized release of  $\text{LNH}_3$  caused a 20% flash and also created aerosols of 10 to 30 microns. An important result of these tests was that vapor clouds hugged the ground while dispersing. Ball (7) has reviewed some problems associated with storage of ammonia and discussed the dispersion of  $\text{NH}_3$  vapor generated from a land spill.

A few experiments in which  $\text{LNH}_3$  was released under water have shown that under suitable conditions (4 to 5 in. depth of release for 4 ml. of  $\text{LNH}_3$ ) almost all of the  $\text{LNH}_3$  dissolved in the water. (8,9) However, other tests produced violent "explosions" which destroyed the test vessel. (10)

A primary objective of our three-stage experimental investigation was to determine the partition ratio, and to study its dependence upon such factors as the size, rate, and orientation of spill, the initial water temperature and

salinity, and the like.

In the first stage (laboratory experiments), quantities of  $\text{LNH}_3$  ranging from 400 to 2600 ml. were released on known quantities of water. See Figure 2. The amount of  $\text{LNH}_3$  dissolved was determined by titration of solution samples.

The second stage was conducted in a small swimming pool (shown in Figure 3) and utilized spill quantities ranging from 1 to 5 gal. The partition ratio for these tests was determined not only from titrations, but by estimation based upon downwind vapor concentration distributions measured with arrays of midget impingers containing boric acid.

A lake served as the site of the third stage of the program. Up to 50 gal. were released on water, and vapor concentration distributions measured were used to estimate partition ratios. See Figure 4.

Details of the experimental apparatus and procedures, the tests conducted, parameters measured, and results obtained were given in an Arthur D. Little report in January, 1974. (11)

Over 90% of the laboratory-scale experiments involving surface spills resulted in partition ratio measurements between 0.65 and 0.82, with a mean of 0.735. Within the experimental scatter, the ratio was found insensitive to quantity, rate, and orientation of spill and virtually independent of water temperature, salinity, air or water motion, or restriction of the  $\text{LNH}_3$ -water reaction area.

A theoretical  $\text{LNH}_3$ -water mixing model, worked out on the basis of adiabatic mixing of  $\text{LNH}_3$  continuously with water, results in the predicted value of 0.73 for the partition fraction. (11) This value is almost the mean value for the experimental data. The agreement between the experimental and theoretical values suggested that the mixing process may be controlled only by thermodynamic parameters.

Measurements conducted during the swimming pool test series, however, resulted in a mean partition ratio of 0.60 for instantaneous spills (with the exception of one erratic data point) and 0.66 for continuous releases. In the lake tests, ratios even lower were estimated from vapor concentration distributions.

These phenomena lead to speculation that, because of the violent boiling, some liquid may be thrown into the vapor phase in the form of fine droplets. This theory is supported by the fact that the more violently interactive instantaneous spills did indeed produce lower partition ratios.

Water temperature rises of  $15^\circ\text{F}$  and  $50^\circ\text{F}$  were observed in the laboratory and lake tests respectively. This difference, together with the observed differences in the partition ratios, suggests that the dynamics of the spill also affects the mixing process.

The size of the boiling zone for instantaneous surface spills was correlated with respect to the spill quantity by the relationship:

$$R = 2.5Q^{0.375} \quad (1)$$

where  $R$  = pool radius in units of feet

$Q$  = volume of ammonia spilled in units of gallons

This relationship is based partly on the experimental data

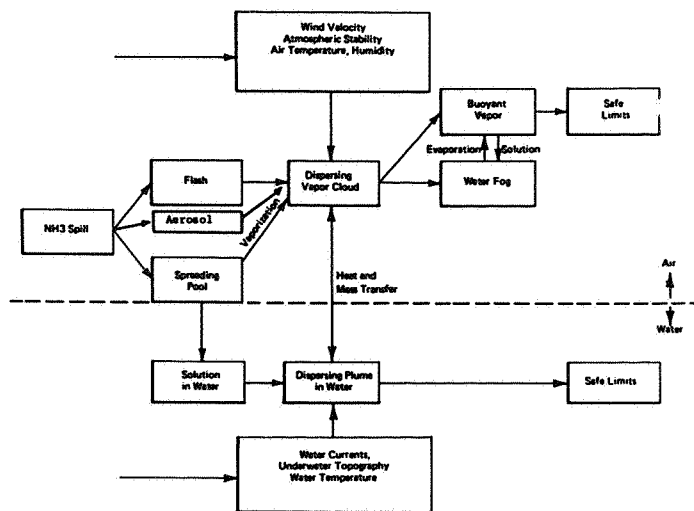


Figure 1. Possible ammonia-air-water interactions.

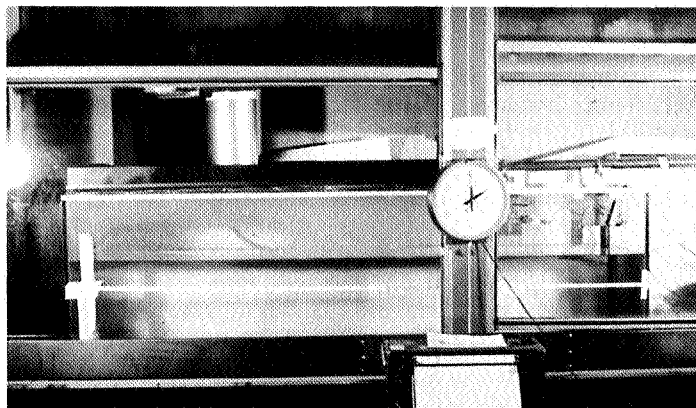


Figure 2. A continuous surface release experiment in progress in the laboratory.

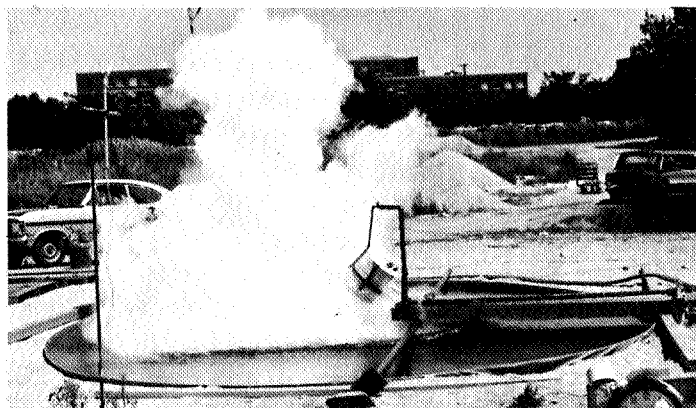


Figure 3. An instantaneous 5-gal. surface spill experiment in progress in the swimming pool.

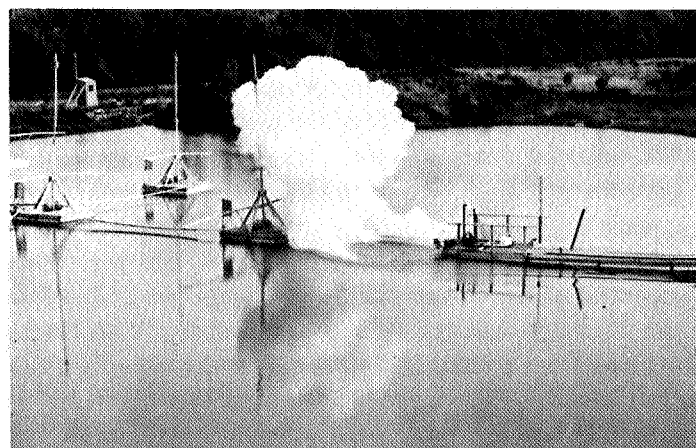


Figure 4. An instantaneous 50-gal. surface spill taking place on the lake.

and partly on the theory of spreading of a vaporizing liquid on another liquid. (12)

The time required for complete dilution or evaporation of the LNH<sub>3</sub> was found to agree well with the following correlation. (12)

$$\tau_e = 0.675 \left[ \frac{V}{G\dot{y}^2} \right]^{1/4} \quad (2)$$

where  $V$  = volume of spill

$\dot{y}$  = linear liquid regression rate (assumed to be a constant)

$G$  = effective gravity =  $g \left( 1 - \frac{\rho_{\text{LNH}_3}}{\rho_{\text{water}}} \right)$

$\tau_e$  = time to complete the evaporation

$\rho_i$  = density of component  $i$ .

Based upon the results of the equation presented for the boiling pool size and the 50-gal. lake tests, it was found that the  $\dot{y}$  was of the order of 2.8 in./min. The time for complete evaporation for these releases is predicted to be 9.5 sec. Times observed in the test series were between 5 and 11 sec.

#### What happens during underwater release

A liquid ammonia barge that sinks in water may eventually release liquid or gaseous ammonia under water depending on the orientation of its cargo tank. If the liquid is released, a plume of liquid ammonia will rise toward the water surface, all the while reacting with the water around it. An objective of this project was to predict the "critical depth" from which all of the rising ammonia (both liquid and vapor) would react with water before reaching the surface.

Concurrently with the surface release test series, experiments were conducted to determine the partition ratios which occur when LNH<sub>3</sub> is discharged under water under various conditions. When the LNH<sub>3</sub> was released at very shallow depths and at low velocity, there was no substantial difference from the mean partition ratio obtained from surface spills. In general, however, when depths were of the order of 10 outlet pipe diameters, the ratio was between 0.85 and 0.95 and closely approached 1.0 as the depth was increased. Higher discharge rates, with their associated greater turbulence and better mixing, also tended to increase partition ratios.

A simple theoretical analysis based on the similarity between a turbulent diffusion flame and a buoyant column of LNH<sub>3</sub> mixing with water, showed that if the discharge flow of the liquid was turbulent and was at a depth greater than about an order of magnitude of the pipe diameter, all of the LNH<sub>3</sub> released would dissolve in water. (11)

A saturated ammonia vapor cloud generated from a spill on water is lighter than air, and rises rapidly when released into the atmosphere, with its rate of rise (height per unit of downwind distance) dependent upon wind speed. The data from the large-scale test series were compared with results predicted from a number of theories of the rise of a maintained buoyant plume and that of a puff of vapor. It was found that a plume rise model, developed by Slawson and Csanady (13) and refined by Hoult, et al., (14) produced results which agreed well with the data.

The equations describing the theory, somewhat modified to account for release of vapor from a virtual source, are:

$$\frac{h}{l_p} = -\frac{\bar{h}}{l_p} + \left( \frac{3}{2\beta^2} \right)^{1/3} \left( \frac{x}{l_p} \right)^{2/3} \left( 1 + \frac{\bar{x}}{x} \right)^{2/3} \quad (3)$$

where  $\bar{x} = \sqrt{\frac{2(b_i c)^3}{3\beta U}}$

$\bar{h} = cb_i/\beta$

$c$  = effective radius fraction, for the finiteness of the source ( $.005 < c < .01$ )

$b_i$  = radius of plume at origin (boiling zone radius/ $\sqrt{2}$ ).

$g$  = gravitational constant

$h$  = height of cloud center above ground level

$l_p$  = buoyancy length in the plume rise =  $\frac{Vg\Delta}{\pi\tau_e}$

$\tau_e$  = time for complete evaporation

$U$  = wind speed

$V$  = volume of vapor generated

$x$  = downwind distance coordinate

$\beta$  = empirical parameter =  $0.5 \leq \beta \leq 2$  (Fay (15) suggests use of  $\beta = 1$ )

$\Delta$  = fractional density defect =  $\left( 1 - \frac{\rho_{\text{vapor}}}{\rho_{\text{air}}} \right)$

When the atmosphere is stably stratified, the limiting height  $h_\infty$  reached by the plume is given by

$$h_\infty = l_p S^{2/3} \quad (4)$$

where  $S$  is the stratification parameter related to the potential temperature gradient in the atmosphere, given by the expression

$$S = \frac{U}{l_p \omega} \quad (5)$$

where  $\omega$  Brunt Vaisalla frequency  $N =$

$$= \sqrt{\frac{g}{T} \frac{\partial \theta}{\partial Z}}$$

$T$  = absolute ambient temperature, and,

$\frac{\partial \theta}{\partial Z}$  = absolute value of the potential temperature gradient in the atmosphere

Equation 3 describes the trajectory of the plume center close to the source, while equation 4 describes the maximum height,  $h_\infty$ , the plume may attain under conditions of inversion. The behavior of a cloud liberated by a massive spill is likely to be more accurately described by puff theory in Morton, et al. (16). However, because of the lack of data for massive spills of LNH<sub>3</sub> and to conform to the findings of the present program, it is suggested that the above model be used until better data become available. It is noted that under very low wind conditions, the vapor cloud rose virtually straight up, taking a classical mushroom shape, and continued rising as it slowly moved downwind.

#### Atmospheric effects on vapor dispersion

The dispersion of vapors from large spills depends to a great extent upon the atmospheric condition. In neutral

and unstable atmospheres, the vapor cloud will rise continuously as it disperses downwind. In stable inverted atmospheres, the cloud center will reach a ceiling height and subsequently disperse almost entirely in the horizontal direction. This will occur because of the lack of an atmospheric mixing process in the vertical direction. From the point of view of ground-level concentrations of vapor, the worst condition during stable atmospheric conditions occurs when fumigation (17) is taking place (i.e., when good mixing occurs between the ground level and a ceiling height, resulting in a uniform vertical concentration distribution).

Because of the short duration in which even massive (instantaneous) spills of  $\text{LNH}_3$  will evaporate and the comparatively long time it takes for the cloud to reach distances of the order of a kilometer or more (in low wind velocities), the spill can be assumed to generate all the vapor instantaneously. To take the finiteness of the source size into consideration, it is assumed that the vapor is generated from a "virtual point source" located five pool diameters upwind. Therefore, in the formulae given below, the dispersion parameters ( $\sigma$ 's) have to be estimated from the location of this virtual point source. The following formulas are used for the two types of atmospheric conditions:

### 1. Neutral and unstable atmospheres:

$$c(x,y,z,t) = \frac{m_y}{(2\pi)^{3/2} \sigma_y^2 \sigma_z} \left[ \exp - \left( \frac{(x-Ut)^2 + y^2}{2\sigma_y^2} \right) \right] \left[ \exp - \frac{(z-h)^2}{2\sigma_y^2} + \exp - \frac{(z+h)^2}{2\sigma_z^2} \right] \quad (6)$$

and the maximum ground level concentration at any  $x$  is given by

$$c_{\text{ground}} = \frac{2m_y}{(2\pi)^{3/2} \sigma_y^2 \sigma_z} \exp \left( - \frac{h^2}{2\sigma_z^2} \right) \quad (7)$$

where  $c$  = concentration in density units

$h$  = height of the center line of the plume at downwind distance  $x$ , calculated from plume theory

$m_y$  = mass of vapor liberated in the spill

$t$  = elapsed time from instant of spill

$x$  = downwind distance coordinate

$y$  = cross-wind distance coordinate

$z$  = vertical distance coordinate

$\sigma_y$  and  $\sigma_z$  = dispersion parameters in the  $y$  and  $z$  direction respectively, Pasquill-Gifford curves. (17)

### 2. Stable atmosphere

An excellent review of the different types of stable atmospheres and their consequences on atmospheric dispersion of pollutants is given by Morton, et al. (16) In the discussion below, two extreme types of stable atmospheres are treated and methods for estimating the ground level concentrations given for each of them.

*Stable: fanning:* In this type of stable atmosphere, the temperature in the atmosphere increases continuously from the ground up. Ammonia vapor released from a spill will rise to a certain height and then spread horizontally, with virtually no vertical dispersion. The ground-level vapor con-

centration in such a case is very small and may be also estimated by using equation 7. However, both the ceiling height  $h_\infty$  and the cloud center height  $h$  should be evaluated and the lower value of the two substituted for the parameter  $h$ . Furthermore, the values of  $\sigma_y$  and  $\sigma_z$  should correspond to those in stable atmospheres (condition F).

*Stable: fumigation:* In this type of stable atmosphere there is a good mixing between the ground and a certain ceiling height. A pollutant cloud tends to disperse downward after rising to this height until the vertical concentration distribution is practically uniform from the ground to the ceiling height.

The following equation is used to estimate maximum ground-level concentrations:

$$c_{\text{ground}}^{\text{max}} = \frac{m_y}{2\pi \sigma_y^2 h_\infty} \quad (8)$$

where  $\sigma_y$  = horizontal dispersion parameter for unstable conditions (generally atmosphere C is used)

The ceiling height for fumigation conditions is an atmospheric parameter and has to be determined from meteorological measurements. The height of the cloud center at times prior to its reaching the ceiling height may be estimated from the plume theory equation. The maximum duration  $\Delta t$  for which the ground concentration level persists above any tolerable concentration  $c^*$  is given by

$$\Delta t = \frac{2\sqrt{2} \sigma_y}{U} \sqrt{\ln \frac{c_{\text{ground}}^{\text{max}}}{c^*}} \quad \left( \begin{array}{l} \text{may be used with} \\ \text{Equations 7 and 8} \end{array} \right) \quad (9)$$

Vapor clouds generated by spills on water rise into the atmosphere in a manner which is dependent upon the wind speed; the higher the wind speed the further downwind the cloud will travel before reaching a given height and vice versa. This is in contrast to Resplandy's (6) land spill experiments, where the cloud hugged the ground and under low wind conditions was observed to fall back toward the ground after a small initial rise.

This suggests that the density of the cloud formed from land spills of  $\text{LNH}_3$  is substantially greater than that from water spills. The difference is probably due to the formation of a much larger fraction of aerosols in land spills. Though not specifically measured in this program, aerosol formation did not take place anywhere near the extent necessary for the cloud to become heavier than air. Figure 5 shows typical calculated results of the above models for a 100-ton  $\text{LNH}_3$  surface release.

### Type of water body has effect on dispersion

Experimental investigation of  $\text{NH}_4\text{OH}$  dispersion was limited to observations of the hydroxide layer formed by spills into a laboratory tank. Because of the stagnant water in the tank, dispersion was primarily due to diffusion and buoyancy driven flow in the horizontal direction. It was found that the spread rate of  $\text{NH}_4\text{OH}$  in still water was of the order of 0.2 ft./sec.

Conditions in navigable waters are quite different. Should a spill occur in a river unaffected by tides, the ammonium hydroxide will be dispersed primarily by stream

turbulence. The degree of accuracy to which one can calculate the concentration of ammonium hydroxide in such waters depends on the degree of precision with which the waterway characteristics are known and incorporated into an analytical model. However, to obtain estimates of the concentration, simplifying assumptions can be made and generalized models developed.

Two models developed for instantaneous spills are presented below. Because of the rapidity with which  $\text{LNH}_3$  spreads and evaporates on water in an instantaneous spill, the source of  $\text{NH}_4\text{OH}$  is considered to be an area source in each. A simplified model for dispersion, in tidal rivers is given in the January, 1974, A. D. Little report. (11)

The equations presented are correct for neutrally buoyant, conservative substances. Though concentrated ammonium hydroxide is lighter than water, the density of water containing low concentrations of it will be very close to that of pure water, and it is felt that inaccuracies resulting from the initial density differences will be small.

#### Near-field model for non-tidal rivers

When  $\text{LNH}_3$  dissolves in water and spreads radially, the  $\text{NH}_4\text{OH}$  formed develops a concentration gradient in the vertical direction. Dye distributions observed in the laboratory experiments indicated that a high concentration initially exists near the water surface, decreasing to a very low value within a depth of a few inches.

Assuming this pool of  $\text{NH}_4\text{OH}$  to be an instantaneous area source of uniform strength, we can show that the concentration at any point downstream is given by

$$c(x,y,z,t) = \frac{2m''}{(4\pi t)^{3/2} \sqrt{e_x e_y e_z}} \int_{x_0=-R}^R dx_0 \int_{y_0=-R}^R dy_0 \left\{ e^{-\frac{(x-Ut-x_0)^2}{4e_x t}} \left[ e^{-\frac{(y-y_0)^2}{4e_y t}} + e^{-\frac{(y+y_0-w)^2}{4e_y t}} + e^{-\frac{(y+y_0+w)^2}{4e_y t}} \right] \left[ e^{-\frac{z^2}{4e_z t}} + e^{-\frac{(z-2d)^2}{4e_z t}} \right] \right\} \quad (10)$$

where  $c$  = concentration in density units  
 $d$  = mean depth of the waterbody  
 $m$  = mass of  $\text{LNH}_3$  that dissolves in water  
 $m''$  = mass of 100%  $\text{NH}_4\text{OH}$  per unit area of

$$\text{spill} = \frac{m}{\pi R^2}$$

$R$  = maximum radius of the  $\text{LNH}_3$  pool  
 $t$  = time at which concentration is desired  
 $U$  = current velocity of waterbody  
 $w$  = mean width of waterbody

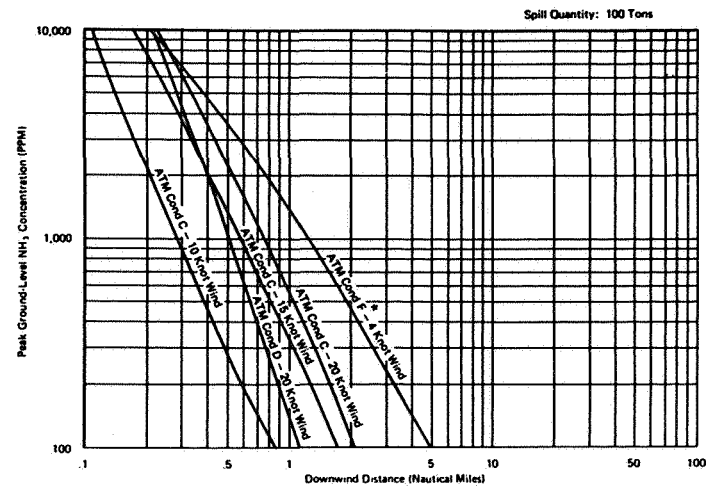


Figure 5. Ammonia vapor concentration vs. distance for 100-ton surface release.

$y_0$  = location of the center of the spill from midstream  
 $x, y, z$  = the downstream, cross-stream (measured from midstream) and depthwise (origin on surface, down is + direction) coordinates of the point at which the concentration is desired

$e_x, e_y, e_z$  = respectively, the longitudinal, lateral, and depthwise turbulent diffusion coefficients in the river. Harleman (18) suggests the use of the expressions in Table 1 for estimating these turbulent diffusivities in a non-tidal river.

Equation 10 is useful in predicting the  $\text{NH}_4\text{OH}$  concentrations very near the spill area. However, it is too complicated to evaluate easily. If we neglect the lateral and longitudinal dispersion terms, it can be shown that the maximum concentration (which occurs on the water surface) at any downstream location  $x$  is given by: (19)

$$c(z=0,t) =$$

$$\rho_l \left[ \frac{h/d + \frac{2}{\pi} \sum_{n=1}^{\infty} \sin(n\pi \frac{h}{d})}{n} \frac{e^{-n^2 \pi^2 \left[ \frac{e_z t}{d^2} \right]}}{n} \right] \text{ for } t_1 \leq t \leq t_2$$

$$0 \text{ for } t < t_1 \text{ and } t > t_2 \quad (11)$$

$$\text{where } t_1 = \frac{(x-R)}{U}$$

$$t_2 = \frac{(x+R)}{U}$$

$$h = \frac{m}{\rho_l \pi R^2}$$

$$\rho_l = \text{density of } \text{LNH}_3$$

Equation 11 gives a constant concentration for a sufficiently large time. In reality, however, this is not the case. Once the vertical distribution becomes uniform, the only mechanism of dilution can be by longitudinal dispersion—a factor which was neglected in the derivation of this equation.

Therefore, for concentration predictions at long times,

**Table 1. Turbulent diffusion coefficients in a river†**

Diffusion Coefficients	Very wide rivers (w/d > 100)	For narrow rivers (w/d < 100)	Remarks
$e_z$	$0.067 u^* d$	$0.067 u^* R_h$	The $e_z$ value is the mean of the vertical distribution given by $e = u^* z(1 - z/d)$
$e_x$	$0.1 e_z$	$0.1 e_z$	
$e_y$	$0.1 e_z$	$0.23 u^* R_h$	

where:  $u^*$  = shear velocity =  $3.3 n U R_h^{-1/6}$

$$R_h = \text{hydraulic radius} = \frac{\text{Stream cross-sectional area}}{\text{wetted perimeter}}$$

$n$  = manning factor  $0.01 < n < 0.04$

$U$  = mean stream velocity

† all quantities are in F.P.S. units

equation 12 is suggested for use: (20)

$$\bar{c}(x,t) = \frac{m}{wd \ 4\pi Et} \quad (12)$$

where  $\bar{c}$  = cross-section averaged concentration in density units

$E$  = longitudinal dispersion coefficient =  $23.3U^*R_h$  (see Table 1).

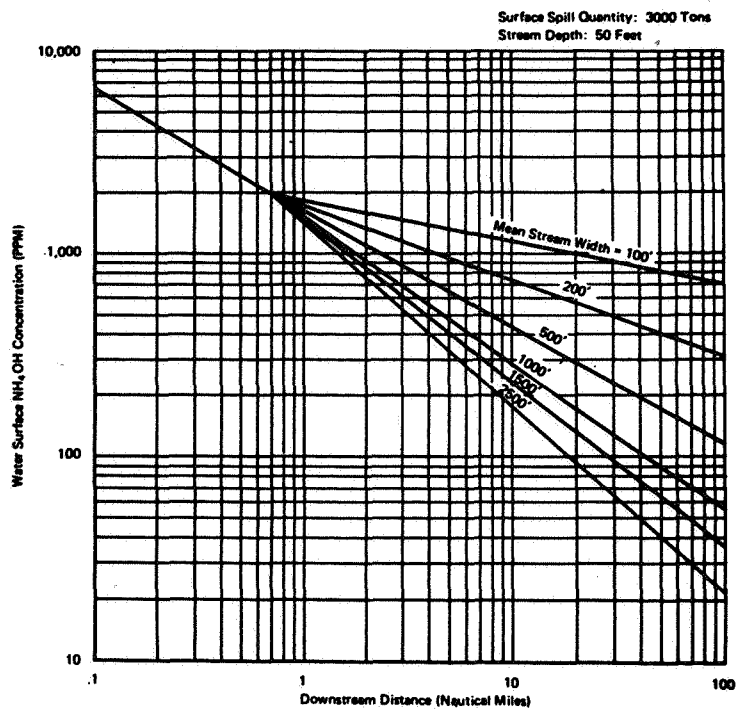
Figure 6 gives an example of the downstream concentrations predicted by these two models. It is noted that certain judgments were made in the region of overlap of the models and the set of curves simplified for providing easily readable and somewhat conservative values for hazard assessment purposes.

It is realized that the above equations do not take into account that the dilution process results in the liberation of ammonia vapor. However, since a solution of concentration less than about 50%  $\text{NH}_4\text{OH}$  can be shown not to release ammonia vapor, except by diffusion processes, (11) and since this concentration will be quickly reached in any given release, the total quantity of vapor liberated will be small.

#### Discussion of data

Analysis of experimental data from three test series resulted in the development of analytical models for use in hazard assessments. Given the various situations under which  $\text{LNH}_3$  potentially may be released either on or under water, it is possible, using the appropriate models, to conservatively approximate downwind or downstream concentrations of  $\text{NH}_3$  vapor or ammonium hydroxide. However, such use requires a full explanation of the major assumptions which were made and their implications on the answers provided.

The vapor dispersion models are point source models of the type which usually predict that the concentration of the vapor is infinity at the spill origin. To compensate for this impossibility, it has been assumed that the source is a



**Figure 6. Ammonium hydroxide concentration vs. distance for 3,000-ton surface spill.**

“virtual point source” moved upwind from the actual spill site. This origin shift results in more realistic vapor concentration predictions at the spill site. However, depending on the weather condition chosen, the concentration predicted might be more or less than what it should be—the density of pure ammonia vapor.

The vapor dispersion models further assume that the surface over which the cloud will travel is perfectly flat. This assumption is reasonable for a cloud traveling over water but may produce conservative predictions whenever obstacles such as buildings or trees are in the travel path. Such obstacles could significantly increase the degree of mixing the cloud experiences.

Also assumed is that all vapor is generated instantaneously. This can never be the case for anhydrous ammonia. Even if liquid should be instantaneously spilled onto water, it will take a finite time (estimated at  $\sim 2$  minutes for a 300-gal. surface release) for the vapor to be liberated. For small leaks in tanks holding large quantities of ammonia, vapor liberation times can be substantially larger. It is to be realized that slower discharge rates result in lower downwind concentrations and correspondingly longer residence times at downwind points.

Use of an instantaneous area source of concentrated ammonium hydroxide, which is assumed to be neutrally buoyant in water, has both advantages and disadvantages. The primary advantage is that the model has not been based upon an infinitely concentrated point source and therefore is more realistic than many similar models in the literature. The drawback results from the assumption that the concentrated solution is neutrally buoyant in water. Given other uncertainties and the fact that  $\text{NH}_4\text{OH}$  is fully miscible in water, the error introduced however is small, especially when there is an appreciable current velocity in the water.



The far-field model for non-tidal rivers only takes longitudinal dispersion in account. The effect of dispersion in the lateral direction is small, but incorporating it into a model would give slightly less conservative answers.

The largest spills conducted during this investigation involved  $\text{LNH}_3$  quantities of 50 gal. Even though this represents the largest spills on water ever conducted to date, it is small compared to the amounts for which the models developed from the data may be utilized. For this reason, whenever an assumption was made it was made in the conservative direction, and it is also for this reason it is cautioned that the models may not fully represent the actual phenomena in the event of a large spill.

### Conclusions

An experimental investigation was undertaken to study the phenomena following the spill of anhydrous liquid ammonia ( $\text{LNH}_3$ ) on water. Some of the major findings of the project are:

1. For large surface spills, the partition ratio depends on the spill dynamics and varies between 0.5 and 0.6 (closer to the latter) for instantaneous release on the surface. For slow, continuous release on the surface, partition ratio values tend to be as high as 0.66. For small spills under controlled laboratory conditions, the partition ratio values are between 0.65 and 0.82, with a mean of 0.735.

2. Very little vapor liberation occurs in the case of underwater release at depths greater than 10 discharge outlet diameters.

3. In the case of large surface spills, the reaction is extremely rapid and results in liberation of a dense fog of vapor, possibly containing a fraction of aerosols, though not a large enough fraction to make the density of the cloud greater than that of air.

4. The vapor cloud formed from spills on water is very buoyant and rises as it travels downwind. The rate of rise depends on the wind velocity. The path of the cloud can be estimated with reasonable accuracy by existing plume theories. Because of the rapid rise in low wind, the toxic hazard at ground level is smaller under low wind than for high wind conditions.

5. Based on the analysis of spread of other cryogenes on water, we expect that a 0.375 power relation with quantity for boiling pool size prediction is appropriate for massive "instantaneous" spills of  $\text{LNH}_3$ .

6. The ammonium hydroxide initially formed at the boiling zone stays close to the top of the water surface and spreads radially at about 0.2 ft./sec.

7. A reasonable estimate of the partitioning for a massive spill on the water surface would be 0.6 into water and 0.4 into vapor.

### Acknowledgement

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