Fate and transport of ammonia spilled from a barge

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1. Introduction

Hazardous materials that are used as raw materials in chemical processes are transported throughout the world by trucks, rail cars, pipelines, and marine vessels. Transportation accounts for 40% of the reported industrial accidents that have occurred in the world, since 1960 [1]. However, only 13% of the transportation accidents involved marine vessels on coastal and inland waterways. Marine vessels include tankers and barges that carry oil, chemicals, and liquified gases.

Anhydrous ammonia is one of many liquified gases that are transported on barges, that typically hold 2500 ton. Other liquified gases and chemicals that are shipped in bulk include propane, butane, liquified natural gas, chlorine, sulfuric acid, toluene, and sodium hydroxide. Each of the chemicals behave differently on release from containment depending on their storage conditions and physical properties. Effects of these chemicals on human health and the environment depends on their specific chemical and toxicological properties. The fate and transport of chemicals upon release into the environment cannot be generalized. This paper addresses the behavior of anhydrous ammonia after release following a hypothetical barge wreck.

2. Ammonia

Ammonia is a colorless gas with a pungent odor at ambient conditions. Its odor threshold is very low (i.e. 5 ppm) compared to levels at which acute harmful effects occur (i.e. 5000 ppm). Therefore, its smell provides excellent warning and allows quick response.

Ammonia is very soluble in water producing a caustic ammonium hydroxide solution. Because of its solubility it reacts with wet tissues such as eyes and mucuous

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membranes in the nose causing damage to the cornea and/or the respiratory system. For humans, the lethal concentration at which 50% of the exposed population would die after a 30 min exposure ($LC_{50,\ 30\ min}$) is 11500 ppm [2]. According to Withers [3] ammonia concentrations of more than 5000 ppm can cause severe effects in vulnerable members of the population. For the purposes of dispersion modeling, discussed in section 5, we have chosen 5000, 2000, and 250 ppm as the concentration levels of concern for identifying vulnerable zones. These concentration levels are intended to be equivalent to the Emergency Response Planning Guidelines (ERPG) concentrations developed by the American Industrial Hygienists Association.

Ammonia is less dense than air at ambient temperatures. Even at its boiling point of − 33 °C its vapor density (0.867 kg/m³) is less than that of air at 25 °C (1.183 kg/m³). Liquid ammonia boils at atmospheric conditions, and it can form a buoyant or denser-than-air mixture depending on release conditions. A dense cloud can form when there is substantial entrainment of fine liquid droplets (aerosol) that rapidly mix with air and cool below the ambient boiling point (subcool).

During transportation in a barge, anhydrous ammonia is stored as a refrigerated liquid at atmospheric pressure. If the barge were involved in a collision that ruptured the container, except for a small fraction that will flash, most of its contents would spill into the water. The behavior of ammonia in this hypothetical accident scenario is discussed in the next section.

3. Spill model

Ammonia barges, with relief valves set typically at 10 psig, carry ammonia at temperatures as warm as − 22 °C. If a barge wreck and instantaneous failure occurred, under these conditions the entire contents (2500 ton) of ammonia at − 22 °C would be released. Approximately 4% of the ammonia will immediately flash upon release to atmosphere, leaving the remainder as liquid at its normal boiling point.

Liquid ammonia, with a density of about 0.684 g/cm³ at the normal boiling point, is buoyant in water, and fully miscible. Therefore, the liquid spill will rapidly spread across the surface of the river while it is boiling and mixing with the water. A model for miscible buoyant spills, based on material balance equations for a control volume consisting of the ammonia remaining in the liquid phase plus the water which has been entrained into the spill by turbulent mixing, was developed for the United States Coast Guard [4]. Called the HACS-R model, it assumes that the spill control volume is well mixed and cylindrical in shape. The model was developed by analogy to heavy gas cloud dilution models.

The HACS-R model has been validated experimentally for buoyant spills using ethanol in water. Good agreement between the modeling and experimental results were obtained [4]. The HACS-R model includes the effect of vaporization of low volatility spills using a mass transfer coefficient. In the case of ammonia, the model must be enhanced to account for boiling, and after boiling stops, to account for rapid evaporation. Further, in case of an accidental release, the initial shape is unknown and it is necessary for a given spill volume to run the model with different spill radii to

examine the sensitivity. Once the volume and radius are specified, the initial depth of the spill is fixed.

This paper presents an extensive enhancement of the HACS-R model to account for the boiling and rapid evaporation of ammonia from the mixture. Equations that are equivalent to those in the HACS-R documentation have an "H" affixed to the equation number. Equations used in the enhanced ammonia model do not.

At any given time, the depth of the spill h_s can be computed from the total mass of the spill and the mixture density. The subscript 1 denotes water and 2 denotes ammonia.

$$h_s = \frac{M_1 + M_2}{\pi \rho_m r^2} \tag{1H}$$

The model is invalid if the spill depth exceeds the river depth. The mixture density is computed neglecting any volume change on mixing.

$$\frac{1}{\rho_m} = \frac{x_1 V_{L1} + x_2 V_{L2}}{M_{wm}} \tag{2H}$$

In this equation, the mole fractions are

$$x_1 = \frac{M_1/M_{w1}}{(M_1/M_{w1}) + (M_2/M_{w2})} \tag{3}$$

$$x_2 = \frac{M_2/M_{w1}}{(M_1/M_{w1}) + (M_2/M_{w2})} \tag{4}$$

and the molecular weight of the mixture is

$$M_{wm} = x_1 M_{w1} + x_2 M_{w2} \tag{5}$$

The spill radius increases with time as a result of buoyancy driven flow in the gravity inertia regime.

$$\frac{dr}{dt} = 1.3 \sqrt{g h_s (\rho_w/\rho_m - 1)} \tag{6H}$$

Eq. (6H) shows how the spreading rate depends on the mixture density ρ_m, through its effect on the gravity wave speed. The mixture density changes with time as water is mixed into the spill. The density of water is ρ_w. The rate of change of the mass of water in the spill is given by

$$\frac{dM_1}{dt} = W_1 - W_{e1} \tag{7}$$

The HACS-R model gives the rate of entrainment of water into the spill through the bottom and side of the cylindrical spill as

$$W_1 = \pi \rho_w r^2 [u_{bot} + 2(h_s/r) u_{side}] \tag{8H}$$

The entrainment velocities represent the rate of mixing at the spill boundaries caused by turbulent diffusion. The HACS-R model obtains these velocities from the following

expressions:

$$u_{\text{side}} = \frac{2(C_f \, dr/dt)^2}{(dr/dt)_{t=0}} \tag{9H}$$

The friction coefficient C_f, which is inversely proportional to the Chèzy coefficient in the standard Manning formula for open-channel flow, is given by

$$C_f = 3.807 n/R_h^{1/6} \tag{10H}$$

where n is the river channel roughness and R_h is the hydraulic radius of the river. The entrainment at the bottom of the spill is given by

$$u_{\text{bot}} = 1.3 \frac{u^*}{6.0 + 0.25 N_{Ri}} \tag{11H}$$

where u^* is the friction velocity and N_{Ri} is the Richardson number. The Richardson number is a ratio of the square of the gravitational spreading rate to the square of the frictional velocity. It quantifies the damping of vertical turbulent mixing by opposing buoyant forces. The friction velocity depends on the current, on R_h and on n. Because the light spill is more stable on top of denser water, turbulence at the boundary is damped. This damping is very strong in the case of an ammonia spill. The friction velocity is estimated from

$$u^* = 3.807 n u/R_h^{1/6} = C_f u \tag{12H}$$

and the Richardson number is

$$N_{Ri} = 0.59 \left(\frac{dr/dt}{1.3 u^*} \right)^2 \tag{13H}$$

A material balance on ammonia gives

$$\frac{dM_2}{dt} = -W_{e2} \tag{14H}$$

In Eqs. (7) and (12H) appear the rates of vaporization of water and ammonia, W_{e1} and W_{e2}, respectively. For ammonia spills, computation of these terms is more complicated than in the original HACS-R model. While the spill is boiling, the total boiling rate

$$W_e = W_{e1} + W_{e2} \tag{15}$$

is determined from an energy balance and the constraint that at all times the bubble point of the mixture equals one atmosphere. This means that boiling occurs as fast as the water entrained into the spill can supply the enthalpy required for vaporization. Neglecting PV terms for liquids the energy balance on the spill becomes

$$\frac{dH_s}{dt} = W_1 h_w - W_e h_v \tag{16}$$

where H_s is the total enthalpy of the spill, h_w is the enthalpy per unit mass of pure water, and h_v is the enthalpy per unit mass of the bubble point vapor which is boiling out of the spill.

During the integration of the time-dependent equations, the algorithm for finding the boiling rate W_e is a pair of nested Newton–Raphson iterations. A boiling rate is guessed and used in energy balance Eq. (16) to determine the total enthalpy of the spill at the end of the time step, and in the material balances to determine the composition and total mass of the spill at the end of a time step. From the total enthalpy and composition the temperature of the spill is computed by Newton–Raphson iteration using the known relations between pure component enthalpies and temperature, and the enthalpy of mixing as a function of temperature and composition. Once the temperature is known, bubble point pressure and composition can be computed. A Newton–Raphson procedure is used to adjust the boiling rate until the calculated bubble point pressure equals one atmosphere.

Using thermodynamic models for ammonia/water mixtures, the bubble point pressure P is calculated to satisfy

$$\sum_{i=1}^{2} P_i = P \tag{17}$$

where the partial pressures of ammonia and water are given by

$$P_i = P_i^v \gamma_i x_i \Phi_i' \exp\left(\frac{V_{Li}}{RT}(P - P_i^v)\right)/\hat{\Phi}_i \tag{18}$$

In Eq. (18), P_i^v is the vapor pressure, γ_i is the activity coefficient, Φ_i' is the pure component liquid saturation fugacity coefficient, V_{Li} is the pure component liquid molar volume, and $\hat{\Phi}_i$ is the mixture fugacity coefficient in the vapor, all for the component i. The activity coefficients are obtained from a three-constant Redlich–Kister equation, with the constants determined from vapor–liquid equilibrium data measured between 313 and 589 K at Wiltec Research Co., Inc., Provo, Utah. Extrapolation to the lower temperatures at which the spill boils at atmospheric pressure was needed. Comparison of the normal boiling point temperature–composition data in Perry's Handbook [5] with extrapolated model predictions showed very good agreement. The fugacity coefficients are computed using the Peng–Robinson equation of state. The Peng-Robinson equation is also used for vapor phase enthalpy departure calculation. When the solution of Eqs. (17) and (18) yield $P = 1$ atm, then the correct boiling rate has been determined. Note that the component boiling rates W_{ei} are determined from the total boiling rate W_e and the bubble point composition. The boiling vapor mole fractions are given by

$$y_i = \frac{P_i}{P} \tag{19}$$

The concentration of ammonia in the spill drops because of dilution by water entrainment and boiloff of ammonia. Eventually, a condition is reached where the

bubble-point pressure drops below atmospheric pressure and boiling stops. At this point, the vaporization of ammonia is now controlled by mass transfer across the gas–liquid interface at the top of the spill. Mass transfer controlled evaporation is much slower than boiling; however, it is important to estimate this rate to determine whether significant airborne source term exists after boiling stops. Mass transfer across the interface occurs in two steps in series from the bulk liquid to the interface and from the interface to the bulk air. Vapor liquid equilibrium exists only at the interface. Neglecting any evaporation or condensation of water, mass transfer coefficients are for transfer of ammonia in a nontransferring medium. The molar flux of ammonia (mol per unit time per unit area) from the bulk liquid to the interface is given by

$$N_2 = \frac{k_{x0}}{x_{1\text{lm}}}(x_2 - x_2^{\text{i}}) \tag{20}$$

where $x_{1\text{lm}}$ is the log mean mole fraction of water between the bulk liquid and the interface, and x_2^{i} is the mole fraction of ammonia at the interface. The symbol k_{x0} is the mass transfer coefficient at infinite dilution. It is estimated from the friction velocity in the river according to the Colburn analogy between mass transfer and momentum transfer.

$$St = \frac{f}{2} Sc_L^{-2/3} \tag{21}$$

$$\frac{k_{x0} M_{\text{wm}}}{u \rho_m} = \frac{f}{2} Sc_L^{-2/3} = \left(\frac{u^*}{u}\right)^2 Sc_L^{-2/3} \tag{22}$$

$$k_{x0} = \left(\frac{\rho_m}{M_{\text{wm}}}\right) \frac{u^{*2}}{u \, Sc_L^{2/3}} \tag{23}$$

The Schmidt number Sc_L for ammonia in water was conservatively taken to be its value at room temperature, even though spill temperatures will be considerably colder.

The flux from the bulk liquid to the interface must match that from the interface to the bulk air, given by

$$N_2 = k_{G0} \frac{P_2^{\text{i}}}{P_{\text{alm}}/P} \tag{24}$$

where P_{alm} is the log-mean partial pressure of air between the interface and the bulk air and P_2^{i} is the partial pressure of ammonia in air at the interface, which is in equilibrium with x_2^{i}. The infinite dilution mass transfer coefficient was estimated from a turbulent boundary layer equation by Sherwood et al. [6]. In the present notation, this equation becomes

$$k_{G0} = 0.037 \, u_{\text{w}} \, Re^{-0.2} Sc_a^{-2/3}/R T_a \tag{25}$$

where Re is the Reynolds number based on the wind velocity u_{w}, the spill diameter $2r$, T_a is the air temperature, and Sc_a is the Schmidt number for ammonia diffusing in air.

Eq. (25) is valid up to a Reynolds number of 300000. Except in very calm air, the Reynolds number for air flowing over a large spill will be much greater than 300000. Therefore, a very conservative choice was made to use the mass transfer coefficient evaluated at $Re = 300000$ whenever $Re > 300000$. In all the case study calculations, a wind speed of 10 ft/s was used for evaporation estimates, which is conservative because less evaporates at lower wind speeds.

A Newton–Raphson iterative procedure was used to find the unknown interface composition for which the fluxes calculated from Eqs. (20) and (24) matched. Results showed that the interface composition was very close to the bulk spill composition, indicating that most of the mass transfer resistance is in the gas phase. Furthermore, the calculated evaporation rates were much lower than the boiling rates, typically two to three orders of magnitude in this case study. Once boiling stops, the generation of significant airborne ammonia is essentially finished.

4. Emissions estimate

Calculations of the fate of instantaneous spills from a barge wreck into a river were carried out using the model equations above. A Fortran program was written to solve the equations. The following properties were assumed for a typical large river:

Width   300 ft,
Depth   20 ft,
Current   1–2 ft/s,
Roughness   0.01–0.03 ft$^{1/6}$,
Temperature   10°–20°C.

The roughness values correspond to a very smooth channel at 0.01 ft$^{1/6}$ and a straight stream at 0.03 ft$^{1/6}$. The most uncertain of the above values were varied to determine the sensitivity of the modeling results. Fig. 1 graphically illustrates the results for the five cases discussed below.

The maximum quantity which could be spilled in a single barge wreck is 2500 ton. In the worst case, the ammonia temperature in the barge would be $-22\,°C$. The first case (Case 1) considered was for a current of 1 ft/s, a roughness of 0.01 ft$^{1/6}$ and a water temperature of 10 °C. The spill will of course never be perfectly cylindrical, and its effective initial radius is not well defined and depends on the manner in which the barge would break open. For Case 1, a spill radius of 100 ft was chosen.

In Case 1, of the initial 2500 ton spilled at $-22\,°C$ about 190000 lb or 96 ton immediately flashes to vapor, leaving 2404 ton as boiling liquid. The initial depth of the spill is 3.6 ft. The spill boils for about 400 s, during which time the spill radius has spread to a calculated value of 854 ft and its depth has reduced to 0.6 ft. Note that the calculated radius is much larger than the width of the river. In reality, then, the shape of the spill would shift from cylindrical to rectangular. To a first approximation, the spill would have a similar volume, concentration, and boiloff rate as the equivalent cylindrical spill. Constrained by the river bank, the spill would actually entrain water at a lower rate than an unconfined cylinder. This means that the time period over
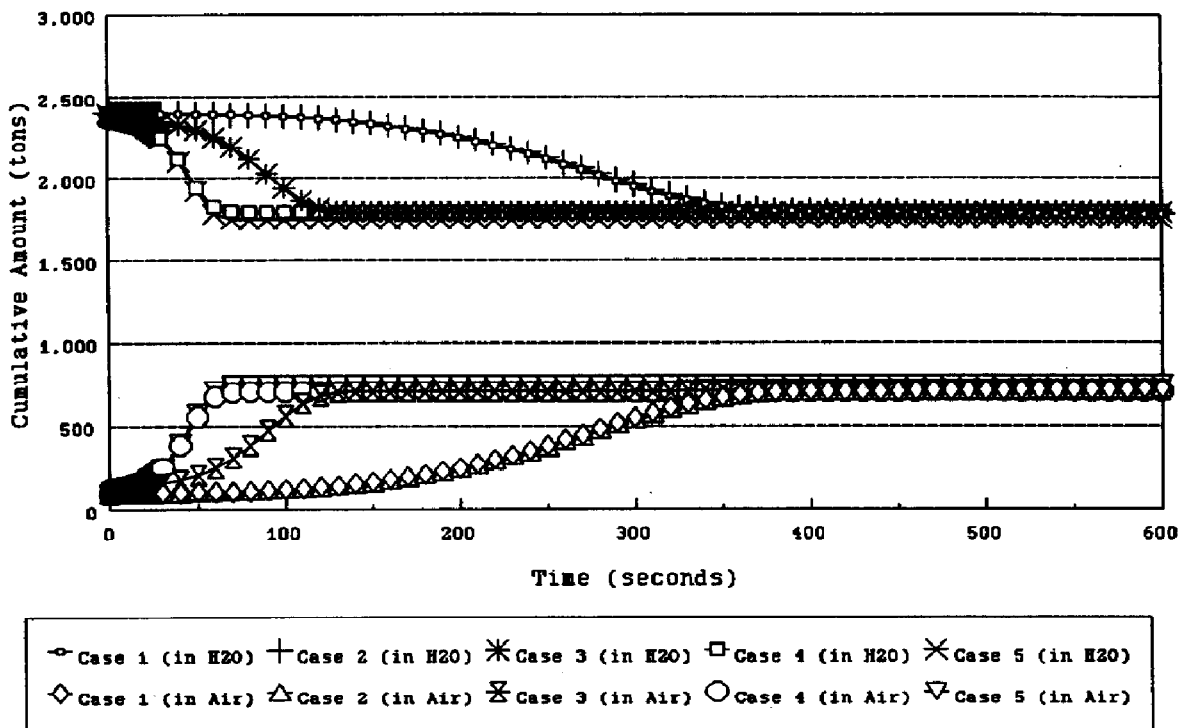
Fig. 1. Results from modeling the fate of 2500 ton of ammonia spilled in a river.

which the ammonia boils off should be longer than calculated, but the total amount boiled off would be the same.

When the boiling stops at about 400 s, the mass of ammonia remaining in the spill is 1795 ton. The total mass of ammonia which either flashed off instantaneously or subsequently boiled off is 705 ton, about 28% of the initial 2500 ton spill. After the boiling stops, ammonia continues to evaporate very slowly under mass-transfer controlled conditions. Beyond that point, the evaporation rate is essentially zero. By accounting for mixing of the spill into the river, the airborne source term is cut by a factor of about three compared to pessimistically assuming all the spilled ammonia ends up in the air.

In the second case (Case 2), the assumed initial radius is cut from 100 to 50 ft. Only very small changes in the results are found. This is because buoyancy forces are so large that the initially deeper spill rapidly spreads and very quickly nearly catches up to the 100 ft initial spill radius.

In the third case (Case 3), the 50 ft initial radius is retained but the roughness of the riverbed is increased to 0.03 ft$^{1/6}$. Tripling the roughness cuts the boiling time from 130 to 140 s, or one-third of the previous boiling time, as expected from the linearity of the mixing rate with roughness n. The same mass of ammonia boils off because this is thermodynamically controlled. Only the time to finish boiling changes with mixing rate. In the mass-transfer controlled regime, the evaporation rate is much lower than it

was for the smooth channel. Less than 10 ton evaporate in 8 min after the boiling stops.

In the fourth case (Case 4), the river current is doubled to 2 ft/s. This halves the boiling time from 60 to 70 s. The mixing rate is linear in river velocity. Again, 28% of the initial spill ends up in air.

In the fifth case (Case 5), the river water temperature is increased to 20 °C. Otherwise, conditions are the same as in Case 4. The increased enthalpy of the water enables additional ammonia to boil off. However, 10° of additional sensible heat gives only a small increase in vaporization. Boiling again occurs for 60–70 s, leaving 1750 ton in the liquid compared to 1795 remaining for 10 °C water. The fraction of the initial spill which flashes or boils off is 30%.

In summary, it is evident that key results are rather insensitive to conditions of the spill. The fraction of ammonia spilled from a barge which ends up in the air will be about 30%. The time required for this fraction to vaporize varies from one to just a few minutes. Griffiths and Kaiser [7] cite experimental studies where typically 60% of the ammonia spilled in water dissolves, with a range of 30–98%. Details of the experimental spill conditions were not given, but it is interesting to note the qualitative agreement with the present simulations.

5. Dispersion modeling

The air transport of an instantaneous puff of ammonia formed after boiling stops is determined by dispersion modeling. Dispersion modeling is used to calculate the downwind concentrations and to provide an estimate of "vulnerable zones" following this hypothetical barge wreck. The vulnerable zones correspond to areas within which the concentrations are higher than the chosen levels of concern (e.g. > 5000 ppm – injury region – for ammonia).

The use of an appropriate dispersion modeling technique depends on the release characteristics and the duration of release. For a good estimate of the downwind concentrations, the "source term" to be used in the dispersion models must be correctly determined. In case of ammonia released from a barge wreck on water, the nature of the source term has been discussed in the previous section.

Ammonia boils and forms a vapor cloud within 60–400 s as shown above. This very rapid vapor generation is modelled as an instantaneous puff to estimate dispersion, as described in the following discussion.

Several computer models are available [8] for modeling the dispersion of ammonia. The dispersion of the ammonia puff was simulated using the TRACE™ model developed by Du Pont Safer Systems [9]. TRACE™ simulates the density-induced gravity spreading, thermodynamic effects due to aerosols, and heat transfer from the surroundings, in addition to the normal diffusion and advection. Its performance has been found to be comparable to other models [10].

Many input parameters are required to use the model, including the total release quantity, meteorological variables, and concentration levels of concern. The most critical meteorological variables are wind speed, atmospheric stability, and surface

roughness. To obtain a conservative estimate of the vulnerable zones a wind speed of 2 mph, E atmospheric stability, and a surface roughness of 0.033 ft was chosen in the analysis. Such low wind speeds and stable atmosphere occur typically at night or early in the morning. These conditions result in greater distances to a given concentration compared to high wind speeds and unstable conditions that are typical of the daytime. F stability was not chosen because it cannot occur near the ground where there are several obstructions. A mixing layer height of 10000 m, that corresponds to no restriction on vertical mixing in a stable atmosphere, was chosen for analysis.

The levels of concern for ammonia chosen for the dispersion modeling are 5000, 2000, and 250 ppm which are 10 min average concentrations. These concentration levels were selected because severe toxic effects can occur from even short exposures. The 10 min average concentrations are conservatively intended to be equivalent to the one hour average Emergency Response Planning Guidelines (ERPG 2 and ERPG 3) concentrations published by the American Industrial Hygienists Association [11].

In TRACE™, the release scenario is specified as consisting of an instantaneous ammonia puff with a size of 750 ton (1.5×10^6 lb) at $-28\,°F$ and an initial radius of 300 ft. The wind speed, atmospheric stability, and surface roughness were specified to be 2 mph, E, and 0.033 ft, respectively. The three downwind distances, corresponding to 5000, 2000, and 250 ppm, are 1.8, 3.8, and 14.4 miles, respectively, as shown in Fig. 2.
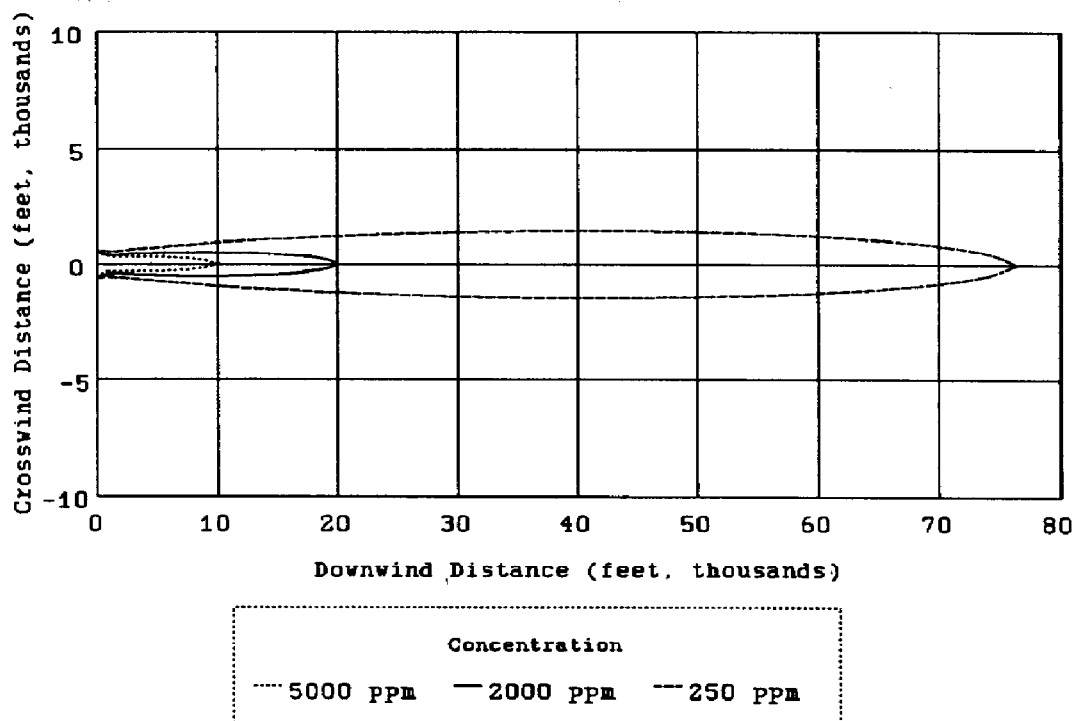

Fig. 2. Concentration isopleths determined from modeling the dispersion of a 750 ton instantaneous ammonia puff at windspeed of 2 mph and E stability.

6. Discussion

A spill evaporation model has been presented in this paper that indicates that of the 2500 ton of ammonia that would be spilled following a barge wreck only 30% becomes airborne. The remaining 70% dissolves in water. The main theme of this paper is the presentation of a methodology for the determination of the the behavior of ammonia and the downwind concentrations following a barge wreck.

The original HACS-R model has been enhanced to account for the boiling and rapid evaporation of ammonia spilled on water. A Fortran program was written to solve the equations presented. The calculations were then carried out for five specific cases to examine the sensitivity of the model to uncertain variables. In all cases a high wind speed of 10 ft/s was assumed for worst case analysis. The amount of airborne ammonia varies from 28% to 30% and the boiling stops in 60–400 s forming a vapor cloud that disperses downwind.

The dispersion of an instantaneous puff of ammonia was simulated using the TRACE™ dense gas dispersion model. In contrast to a high wind speed (10 ft/s) for pool evaporation calculations, a low wind speed (2 mph) was used to obtain a conservative estimate of downwind distances to a given concentration. The distances to the three concentration levels of concern (5000, 2000, and 250 ppm) are 1.8, 3.8, and 14.4 miles, respectively. These distances are much less than would be predicted if it were assumed that all of the ammonia spilled on the water instantaneously vaporized. Even though violent boiling occurs, the rapid spreading and dissolution of ammonia in water has a major impact on the amount of ammonia vaporized.

Nomenclature

C_f	friction coefficient
f	Fanning friction factor
g	acceleration of gravity
h_s	spill height
h_v	vapor enthalpy per unit mass
h_w	water enthalpy per unit mass
H_s	total enthalpy of spill
k_{G0}	gas-side mass transfer coefficient
k_{x0}	liquid-side mass transfer coefficient
M_1	mass of water in spill volume
M_2	mass of ammonia in spill volume
M_{w1}	molecular weight of water
M_{w2}	molecular weight of ammonia
M_{wm}	molecular weight of the spill mixture
n	river roughness
N_2	molar flux of ammonia
N_{Ri}	Richardson number

P	total pressure
P_{alm}	log-mean partial pressure of air
P_i	partial pressure of species i
P_2^i	partial pressure of ammonia at the interface
P_i^v	vapor pressure of species i
r	spill radius
R	gas constant
R_h	hydraulic radius of river
Re	Reynolds number
Sc_a	Schmidt number for ammonia diffusing in air
Sc_L	Schmidt number for ammonia diffusing in liquid
St	Stanton number
t	time
T_a	air temperature, absolute
u	mean river velocity
u^*	friction velocity
u_{bot}	entrainment velocity at bottom of spill
u_{side}	entrainment velocity at side of spill
u_w	wind velocity
V_{Li}	pure component liquid molar volume
V_{L1}	molar volume of liquid water
V_{L2}	molar volume of liquid ammonia
W_1	mass rate of entrainment of water into spill
W_e	total mass rate of vaporization
W_{e1}	mass rate of water vaporization
W_{e2}	mass rate of ammonia vaporization
x_1	bulk water mole fraction in spill
x_{1lm}	log-mean water mole fraction in liquid
x_2	bulk ammonia mole fraction in spill
x_2^i	ammonia mole fraction in liquid at the interface
Y_i	mole fraction of species i in vapor
γ_i	activity coefficient of species i in the liquid
ρ_m	mixture density of the spill
ρ_w	density of liquid water
Φ_i'	pure component liquid saturation fugacity coefficient
$\hat{\Phi}_i$	mixture fugacity coefficient of species i in the vapor

References

[1] P. Haastrup and L. Brockhoff, Severity of accidents with hazardous materials, a comparison between transportation and fixed installations, J. Loss Prevention, 3 (1990) 395–405.
[2] R.D.J. Withers, The Lethal Toxicity of Ammonia. A report to the Major hazards advisory panel, Institution of Chemical Engineers, North Western Branch, UK, 1986.

[3] F. Pederson and R.S. Selig, Predicting the consequences of short-term exposure to high concentrations of gaseous ammonia, J. Hazardous Mater., 21 (1989) 143–159.

[4] F.T. Dodge, J.C. Buckingham and T.B. Morrow, Analytical and Experimental Study to Improve Computer Models for Mixing and Dilution of Soluble Hazardous Chemicals. US Coast Guard Report CG-D-1-83, Department of Transportation, US Coast Guard, Office of Research and Development, Washington, DC, 1982.

[5] R.H. Perry and D.W. Green, Perry's Chemical Engineers' Handbook, 6th Edn., Mc-Graw Hill, New York, 1984, pp. 3-170–3-171.

[6] T.K. Sherwood, R.L. Pigford and C.R. Wilke, Mass Transfer, McGraw-Hill, New York, 1975, p. 201.

[7] R.F. Griffiths and G.D. Kaiser, Production of dense gas mixtures from ammonia releases – A review, J. Hazardous Mater., 6 (1982) 197–212.

[8] S.R. Hanna and P.J. Drivas, Guidelines for Use of Vapor Cloud Dispersion Models, Center for Chemical Process Safety, AIChE, New York, 1987.

[9] DuPont SAFER Systems, 5700 Corsa Avenue, Westlake Village, CA 91362.

[10] Environmental Protection Agency, Evaluation of Dense Gas Simulation Models, EPA-450/4-89-018, US Environmental Protection Agency, Research Triangle Park, NC, 1991.

[11] American Industrial Hygiene Association, Emergency Response Planning Guidelines, American Industrial Hygiene Association, Akron, OH, 1990.