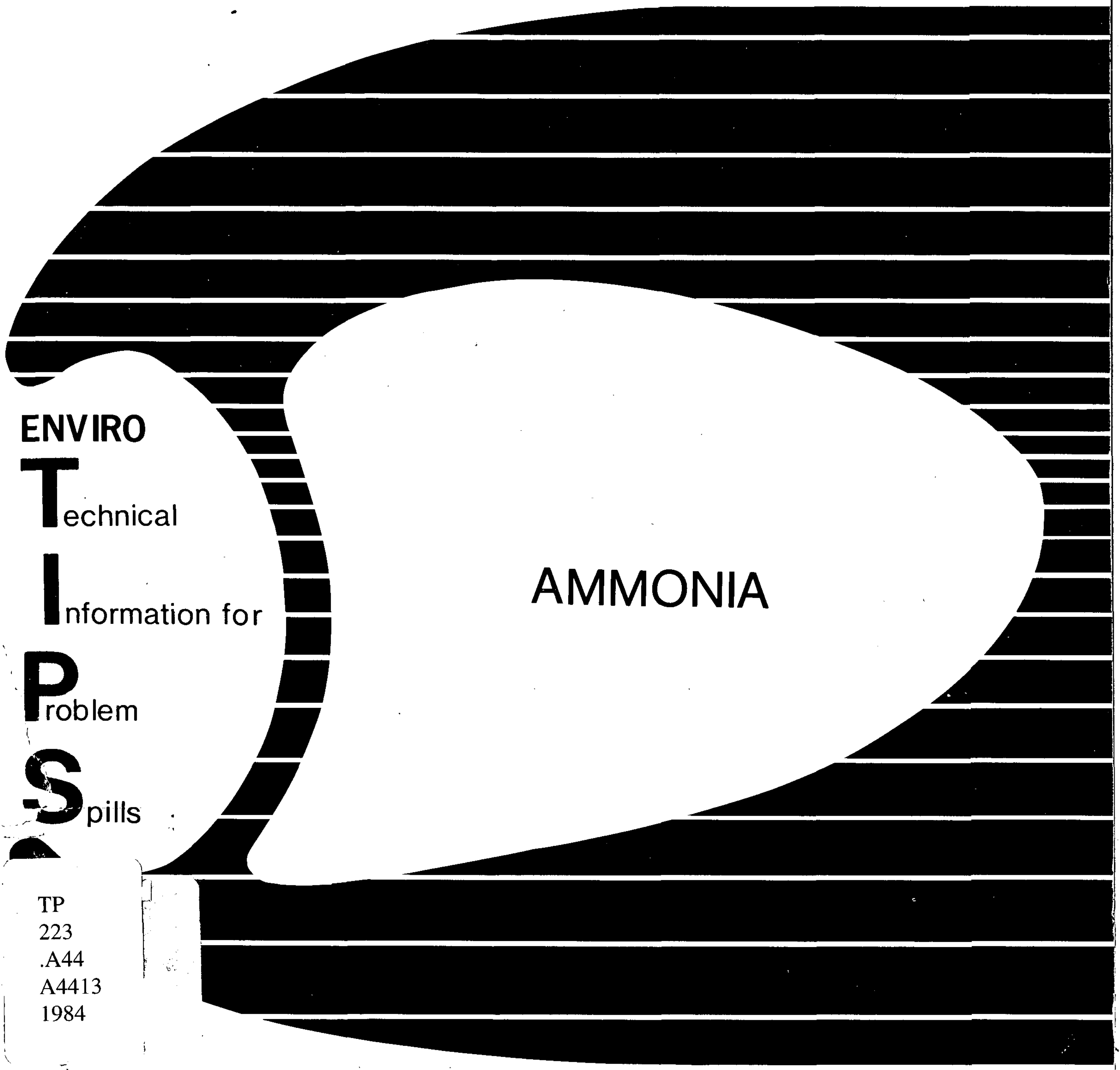
Environment Canada
Environmental Protection Service

Environnement Canada
Service de la protection de l'environnement



ENVIRO Technical Information for Problem Spills

AMMONIA

JULY 1984

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

AMMONIA

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

July 1984

Cat. No. En 48-10/16-1984E
ISBN 0-662-13429-X
BEAUREGARD PRESS LIMITED

FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who rewrote the text, drafted illustrations and incorporated all comments and additions.

The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited. The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 SUMMARY

AMMONIA (NH_3) (Anhydrous and aqueous)

Anhydrous ammonia is a colourless gas with a sharp, penetrating odour and is often shipped in liquefied form. Ammonia is also available as clear to white solutions of various percentages

SYNONYMS

Ammonia Anhydrous, Ammonia Gas, Ammoniac (Fr.)

IDENTIFICATION NUMBERS

UN No. 1005 (anhydrous, liquefied), 2672 (solutions, 10-35 percent), 2073 (solutions, 35-40 percent); STCC No. 4904210 (anhydrous), 4904220 (solutions, >44 percent), 4904221 (ammoniacal liquor); CAS No. 7664-41-7; OHM-TADS No. 7216584

GRADES & PURITIES

Anhydrous; technical, commercial, industrial, refrigeration, electronic, and metallurgical, >99.5 percent purity

Solutions: technical, commercial, 28 to 30 percent

Liquors: >44 percent

IMMEDIATE CONCERNS

Fire: Nonflammable. Danger of explosion in an enclosed space at 16 to 25 percent by volume with air, under certain conditions

Human Health: A severe irritant to skin, eyes and respiratory tract. Toxic by inhalation

Environment: Harmful to aquatic life in very low concentrations

PHYSICAL PROPERTY DATA

State (15°C, 1 atm):	gas
Boiling Point:	-33°C
Melting Point:	-77.7°C
Flammability:	combustible
Vapour Pressure:	888 kPa @ 21°C
Density:	0.68 g/mL @ -33.7 °C
Vapour Density:	0.71 g/L (25°C)
Solubility:	89.9 g/100 mL (0°C)
Behaviour (in water):	dissolves with mild heat release
Behaviour (in air):	may disperse like a heavy gas initially
Odour Threshold Range:	1 to 53 ppm

ENVIRONMENTAL CONCERNS

Spills of liquefied ammonia or of aqueous ammonia solutions will rapidly disperse through the water. Ammonia is toxic to fish and other aquatic life. It is harmful to some species at concentrations as low as 0.4 mg/L (unionized ammonia). In neutral or basic solutions, ammonia will volatilize and escape to the atmosphere. It is a severe irritant to animals due to its corrosive effect on skin, eyes and respiratory system. There is no potential for biological accumulation or food chain concentration.

HUMAN HEALTH

TLV®: 25 ppm (18 mg/m^3)

IDLH: 500 ppm

Exposure Effects

Inhalation: Breathing of vapour causes irritation of nasal and respiratory passages and either immediate or delayed breathing difficulties. Prolonged or severe exposure can cause death

Contact: Gas: Contact to eyes causes severe irritation, redness, tearing, blurred vision and temporary blindness. Vapour on skin can cause irritation, blistering and dermatitis

Liquid: Contact can produce severe eye injury or blindness and skin burns (frostbite)

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Call fire department and notify manufacturer. Evacuate area in case of large leaks or tank puncture. Stop or reduce the discharge and contain spill, if safe to do so. Avoid skin contact or inhalation; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not flammable, but combustible. Use dry chemical or carbon dioxide to extinguish. Cool fire-exposed containers with water. Stay clear of tank ends.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers (dykes or lagoons) to contain spill. Flush area with water and neutralize with dilute acid (if safe to do so)

Water: Contain, if possible, by damming or water diversion

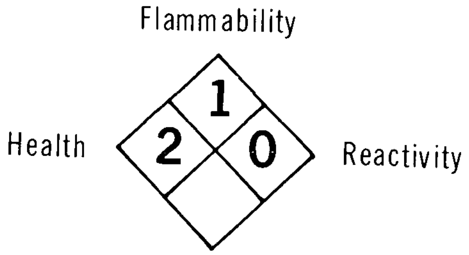
Air: Use water spray to absorb vapours. Control runoff for later treatment and/or disposal

NAS HAZARD RATING

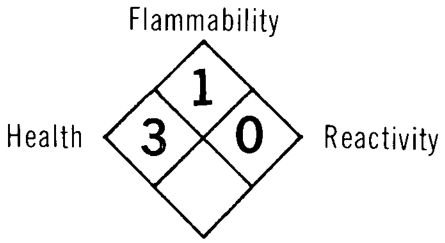
Category	Rating
Fire	1
Health	
Vapour Irritant	4
Liquid or Solid Irritant	2
Poison	2
Water Pollution	
Human Toxicity	2
Aquatic Toxicity	2
Aesthetic Effect	2
Reactivity	
Other Chemicals	3
Water	2
Self-reaction	0

NFPA
HAZARD
CLASSIFICATION

GAS



LIQUIFIED



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Pungent, colourless gas. May be compressed and cooled to a colourless liquid (HCG 1981)
Usual shipping state	Liquefied gas under its own vapour pressure of 787 kPa (20°C) (Matheson 1966)
Physical state at 15°C, 1 atm	Gas
Melting point	Anhydrous: -77.71°C (Kirk-Othmer 1978) $NH_3 \cdot H_2O$: -79.01°C (Cotton 1972) $2NH_3 \cdot H_2O$: -78.84°C (Cotton 1972)
Boiling point	-33.35°C (Kirk-Othmer 1978)
Vapour pressure	888.0 kPa (21°C) (Matheson 1980)
Decomposition temperature	450 to 500°C (HCG 1981)

Densities

Density	Anhydrous Liquefied: 682.8 kg/m^3 (33.7°C) (Matheson 1980) Gas: 0.7067 kg/m^3 (25°C) (Matheson 1980)
Specific gravity	Anhydrous Liquefied: 0.6818 (-33.5°C) (API 1981) 28 percent Solution: 0.8980 (20°C) (Jolly 1964) Gas: 0.5970 (25°C) (Matheson 1980)

Fire Properties

Flammability	Due to its low susceptibility to fire, ammonia is classified by the U.S. DOT as nonflammable (HCG 1981)
Autoignition temperature	651.1°C (NFPA 1978; Matheson 1980)
Burning rate	1 mm/min (CHRIS 1978)
Upper flammability limit	25 percent (HCG 1981; NFPA 1978) 27 percent (0°C) (Ullmann 1975) 28 percent (100°C) (Ullmann 1975)
Lower flammability limit	16 percent (HCG 1981; NFPA 1978) 16 percent (0°C) (Ullmann 1975) 15.5 percent (100°C) (Ullmann 1975)
Burning characteristics	Horizontal flame propagation. Presence of oil or other combustible materials will increase the fire hazard (NFPA 1978)
Heat of combustion	18.6 kJ/g (AAR 1981)
Combustion products	Nitrogen and water (HCG 1981)
Decomposition temperature	450 to 500°C (HCG 1981)

Decomposition products	Nitrogen and hydrogen (HCG 1981)
Explosiveness	Ammonia vapours in confined spaces may produce explosive mixtures. Heated containers may rupture violently (Erco HCM 1981)

Other Properties

Molecular weight of pure substance	17.03 (Kirk-Othmer 1978)
Constituent component (%)	Anhydrous:

Grade	Minimum weight % ammonia
Commercial	99.5
Agricultural	99.7
Refrigeration	99.95
Metallurgical	99.995

Impurities are usually water and oil (HCG 1981)

	Solutions: 0-60 percent ammonia (Kirk-Othmer 1978)
Refractive index	Gas: 1.003 (25°C), 0.817 (-79°C) (CRC 1980) Liquefied: 1.325 (16.5°C) (CRC 1980)
Viscosity	Liquefied: 0.255 mPa•s (-33.5°C) (Matheson 1980) Gas: 0.00918 mPa•s (0°C), 0.00982 mPa•s (20°C) (Matheson 1966)
Interfacial tension with air	Gas: 23.4 mN/m (11.1°C) (CRC 1980) Liquefied: 44.55 mN/m (-40°C) (Matheson 1980)
Liquid interfacial tension with water	54% Solution: 54.37 mN/m (CRC 1980)
Latent heat of fusion	332.2 kJ/kg (-77.72°C) (HCG 1981)
Latent heat of sublimation	1.7 kJ/g (Perry 1973)
Latent heat of vaporization	1367.2 kJ/kg (at boiling point and atmospheric pressure) (Matheson 1980)
Heat of formation	-45.9 kJ/mole (gas at 25°C) (JANAF 1971)
Ionization potential (eV)	10.17 eV (Rosenstock 1977)
Heat of solution	801.1 kJ/kg (infinite dilution) (HCG 1981) 628.0 kJ/kg (40 percent solution) (Kirk-Othmer 1978)
Heat capacity	
constant pressure (Cp)	Liquefied: 4.295 kJ/(kg•°C) (Matheson 1980) Gas: 2.170 kJ/(kg•°C) (Matheson 1980)
constant volume (Cv)	Gas: 1.661 kJ/(kg•°C) (Matheson 1980)
compressibility factor (γ)	Gas: 1.307 (Matheson 1980)
Critical temperature	133.0°C (HCG 1981; Kirk-Othmer 1978)
Critical pressure	11,420 kPa (HCG 1981; Kirk-Othmer 1978)
Coefficient of thermal expansion	3.76 x 10^{-3}/°C (Perry 1973) 50.17 x 10^{-4} (J•cm)/(s•cm^{2}•°C) (10°C) (Matheson 1966)

Dielectric constant	Gas: 1.0072 (0°C) (Matheson 1980) Liquefied: 22.4 (-33.7°C) (Matheson 1980)
Electrical conductivity	Liquefied: 1 x 10^{-9} ohm^{-1} m^{-1} (Jolly 1964)
Thermal conductivity	Gas: 0.02218 W/(m•K) (0°C) (Matheson 1980) Liquefied: 0.5017 W/(m•K) (10°C)
Diffusivity	1.7 x 10^{-5} cm^2/s (Perry 1973)
Saturation concentration	158 mg/m^3 (-6°C) (CRC 1980)
pH of aqueous solution	1 N solution: 11.6 (25°C) (CRC 1980) 0.1 N solution: 11.1 (25°C) (CRC 1983)
Evaporation rate	16.4 $g/(m^2•s)$ (this work)

Solubility

In water	89.9 g/100 mL (0°C) (CRC 1980) 52.9 g/100 mL (20°C) (API 1981)
In other common materials	Soluble in mineral acids, ether and other organic solvents. Solubility in ethanol is 13.2 g/100 mL at 20°C (CRC 1980)

Weight to Volume Conversion Factor

1 ppm = 0.707 mg/m^3 (Verschueren 1977)

Summary of Properties and Behaviour (Cotton 1972; Sisler 1961; Jolly 1964; Kirk-Othmer 1978)

Ammonia (NH_3) is a colourless, pungent, gas with a normal freezing point of -77.8°C and a boiling point of -33.35°C. The ammonia molecule has the form of a pyramid, with the nitrogen atom at the apex and the hydrogen atoms at the corners of the base, which is an equilateral triangle. A comparison of the physical properties of ammonia (e.g., melting and boiling points, heats of vaporization and fusion) with the corresponding values for the hydrogen compounds of the other members of the Group VA elements reveals that the properties of ammonia are abnormal with respect to the others. This is in the same sense that the properties of water and hydrogen fluoride are abnormal with respect to the other hydrogen compounds of their respective groups. These abnormal characteristics can be explained on the basis of intermolecular association by means of hydrogen bonding. This is simply the formation of a bridge between two highly electronegative atoms by means of a proton. Ammonia molecules have a high degree of polarity resulting from the pyramidal structure of the molecule, the polarity of the N-H bond, and the configuration of the charge distribution of the unshared pair of electrons.

Liquid ammonia, a colourless, free-flowing material, is probably one of the most extensively studied nonaqueous solvents and is the most important inorganic solvent besides water. Its good solvent characteristics mainly derive from the high dipole moment of the molecule. The liquid is characterized by a high degree of mobility even at low temperatures and has an unusually high thermal coefficient of expansion. Ammonia self-ionizes according to the following equation:

$$2NH_3 \rightleftharpoons NH_4{}^+ + NH_2{}^- \qquad K_{-50°C} = \left[NH_4{}^+\right]\left[NH_2{}^-\right] = \simeq 10^{-30}$$

$$(K_{-50}(\text{water}) = 10^{-14})$$

Ammonia has a lower reactivity than water towards electropositive metals (hydrogen is not evolved) and actually dissolves many to give a blue solution containing metal ions and solvated electrons. It is a better solvent for organic compounds than water because of its lower dielectric constant and is generally a poorer one for ionic inorganic compounds. Solubility examples include the alkali and alkaline earth metals (except berylium, magnesium and potassium), iodine, sulphur and phosphorus. Most fluorides are not soluble in liquid ammonia. Silver and uranium are only slightly soluble. Most chlorides, except ammonium and berylium, are only slightly soluble or insoluble, whereas bromides are generally more soluble, and iodides are more or less soluble. Oxides, hydroxides, sulphates, sulphites and carbonates are insoluble. Ammonium nitrate (and nitrates in general) and urea are soluble in both anhydrous and aqueous ammonia. This latter property makes the production of fertilizer nitrogen solutions possible. Soluble organic compounds include amines, nitro compounds and aromatic sulphonic acids.

Ammonia is extremely soluble in water. Above 0°C, ammonia and water are miscible in all proportions; however, at lower temperatures, two crystalline hydrates are formed ($NH_3 \bullet H_2O$, m.p. -79.01°C and $2NH_3 \bullet H_2O$, m.p. -78.84°C). There is some evidence of the existence of a dihydrate ($NH_3 \bullet 2H_2O$) that melts incongruently at -98°C in the region of the eutectic between ice and ammonia monohydrate. The ammonia and water molecules in the compounds are linked by hydrogen bonds; the substances contain neither ammonium ($NH_4{}^+$) and hydroxide (OH^-) ions nor discrete NH_4OH molecules. Ammonia is probably hydrated in a similar manner in aqueous solution. Aqueous ammonia solutions are commonly referred to as solutions of the weak base ammonium hydroxide (NH_4OH); however, there is no evidence that undissociated ammonium hydroxide exists. Solutions of ammonia in water are best described as NH_3(aq.), with the equilibrium shown as

$$NH_3(\text{aq.}) + H_2O \rightleftharpoons NH_4{}^+ + OH^-, \qquad K_{25°C} = \left[NH_4{}^+\right]\left[OH^-\right]/\left[NH_3\right] = 1.81 \times 10^{-5}$$

A 1 M solution of ammonia is only 0.0042 M in NH_4^+ and OH^-. Considerable heat is evolved during the dissolution of ammonia in water (ΔH_{soln} = ≃2 180 kJ/kg). The reaction between ammonia and water is reversible; as such, its solubility decreases rapidly with increasing temperature. As can be derived from the equilibrium constant shown above, aqueous ammonia is a comparatively weak base. It will precipitate metallic hydroxides from solutions of their salts and form complex ions in excess ammonia solutions.

Ammonia is stable at ordinary temperatures but decomposes to hydrogen and nitrogen at elevated temperatures. The decomposition rate is affected by the nature of the surface with which the gas is in contact. Glass, for example, is very inactive, whereas porcelain and pumice have a distinctly accelerating effect, and metals such as iron, nickel, osmium, zinc and uranium even more so. The dissociation begins at about 450-500°C at atmospheric pressure; in the presence of a catalyst, it begins at temperatures as low as 300°C and is nearly complete at 500-600°C. Even at 1 000°C, however, a trace of ammonia remains.

Ammonia is a fairly reactive gas; it reacts readily with a large variety of substances. High temperature oxidation to form nitrogen and water is one of the more important reactions. This reaction can be effected by many metal oxides, for example copper (II) oxide (CuO). Other more powerful oxidizing agents react similarly, e.g.,

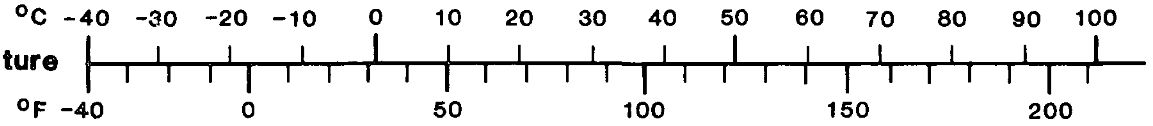
$$2NH_3 + 2KMnO_4 \longrightarrow 2KOH + 2MnO_2 + 2H_2O + N_2$$

Chlorine reacts with ammonia to give nitrogen and ammonium chloride (NH_4Cl); under ideal conditions, chloramines (NH_2Cl, $NHCl_2$) may be formed. In the presence of excess chlorine, however, chloramines and nitrogen trichloride (NCl_3) are favored. The latter is a yellow, oily material that can spontaneously decompose explosively. The neutralization of acids is of commercial importance as three major fertilizers are made from ammonia (ammonium nitrate, sulphate and phosphate). Another compound of major industrial importance, urea (NH_2CONH_2), is formed by the reaction of ammonia and carbon dioxide.

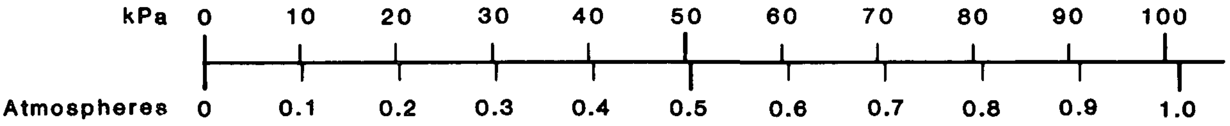
Other reactions of possible significance to emergency response personnel are ammonia plus phosphorus vapour at red heat (possible fire conditions) to give nitrogen and phosphine (PH_3); sulphur vapour and ammonia to give ammonium sulphide ($(NH_4)_2S$) and nitrogen; sulphur with anhydrous liquid ammonia to give hydrogen sulphide (H_2S) and tetranitrogen tetrasulphide (S_4N_4); and ammonia and carbon at red heat to give ammonium cyanide (NH_4CN). The compounds mentioned are either poisonous, unstable, can react with air to produce other noxious materials, or are all of the aforementioned.

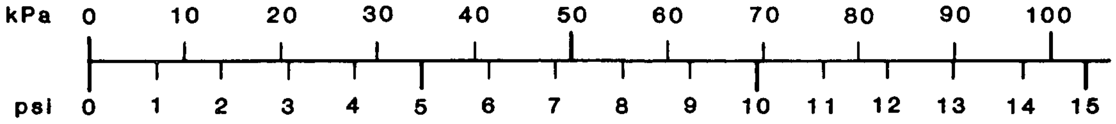
CONVERSION NOMOGRAMS

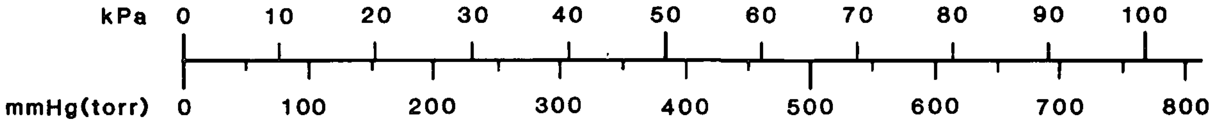
Temperature



Pressure 1 kPa = 1,000 Pa







Viscosity

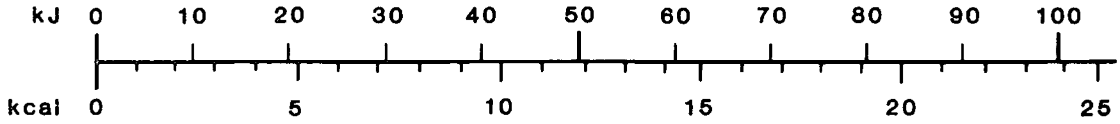
Dynamic 1 Pa·s = 1,000 centipoise (cP)

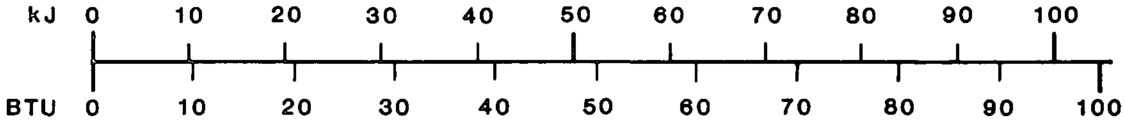
Kinematic 1 m^2/s = 1,000,000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1,000 J





Density

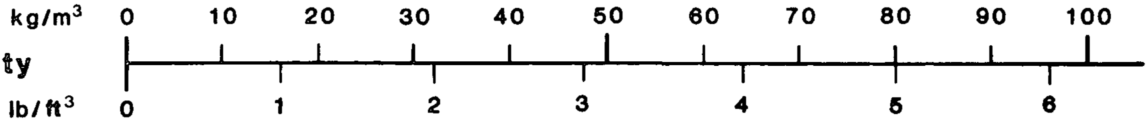


FIGURE 1

AMMONIA (Aqueous Solutions)

PHASE DIAGRAM FOR THE $NH_3.H_2O$ SYSTEM

Reference: SISLER 1961; JOLLY 1964

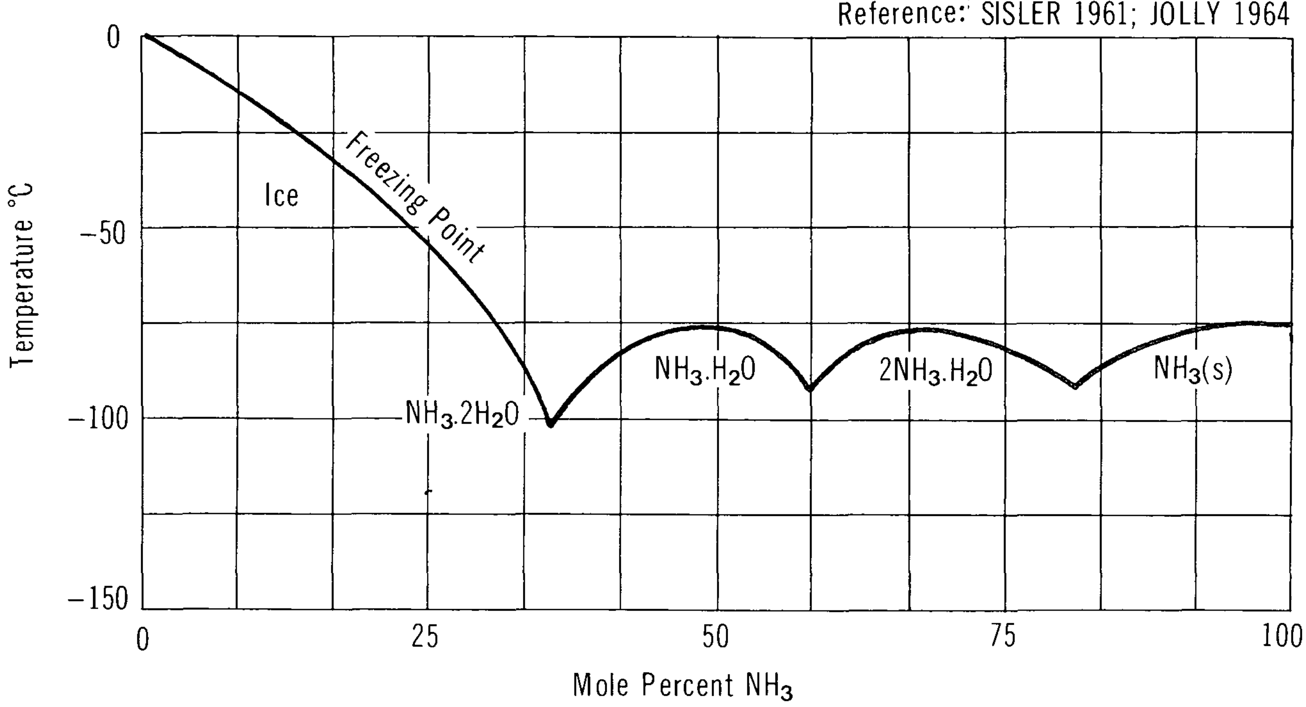


FIGURE 2

AMMONIA (Aqueous Solutions)

LIQUID DENSITY

Reference: KIRK-OTHMER 1978

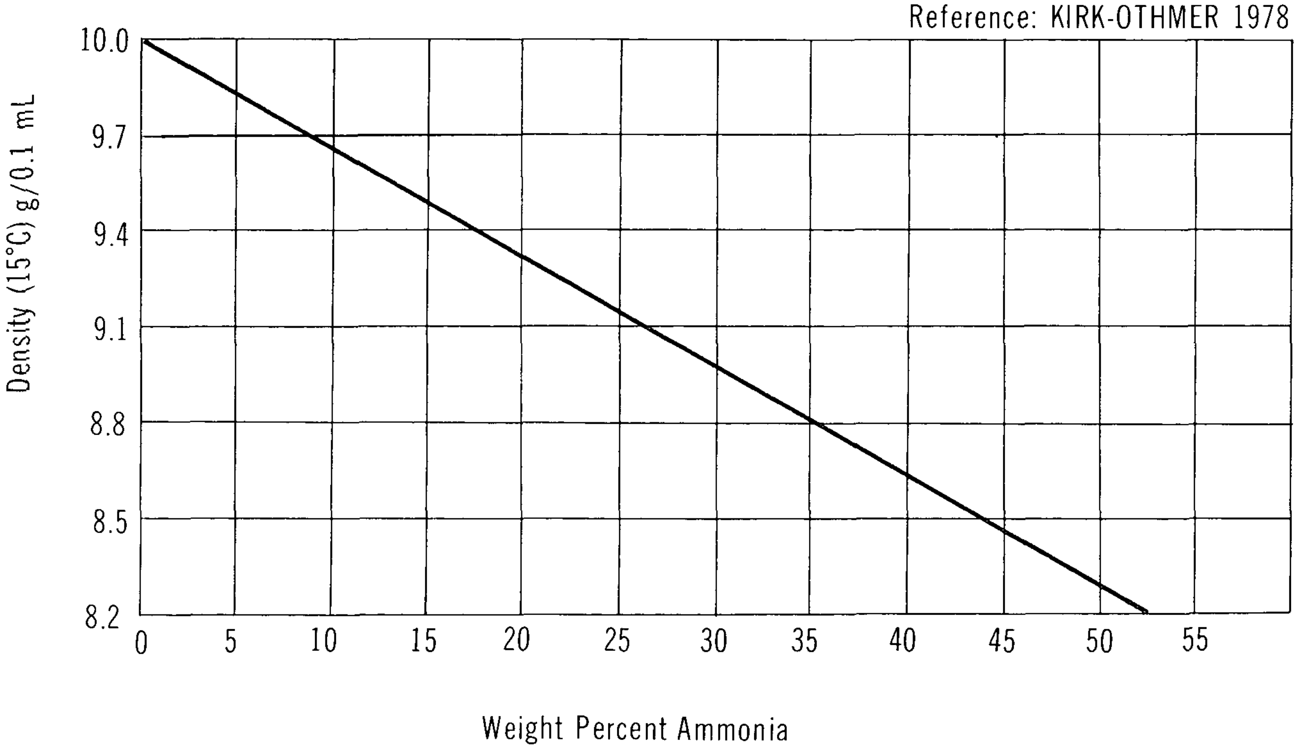


FIGURE 3

AMMONIA (Liquified anhydrous)

LIQUID DENSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

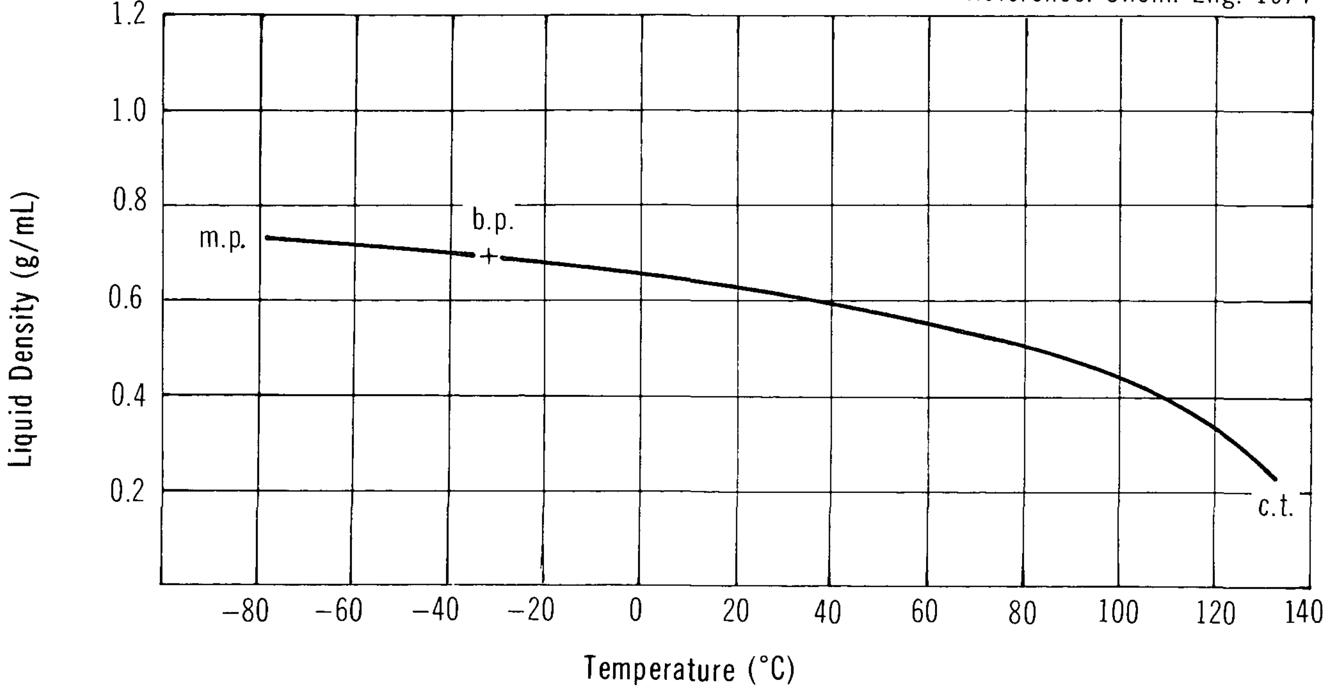


FIGURE 4

AMMONIA

VAPOUR DENSITY VS TEMPERATURE

Reference: MATHESON 1966

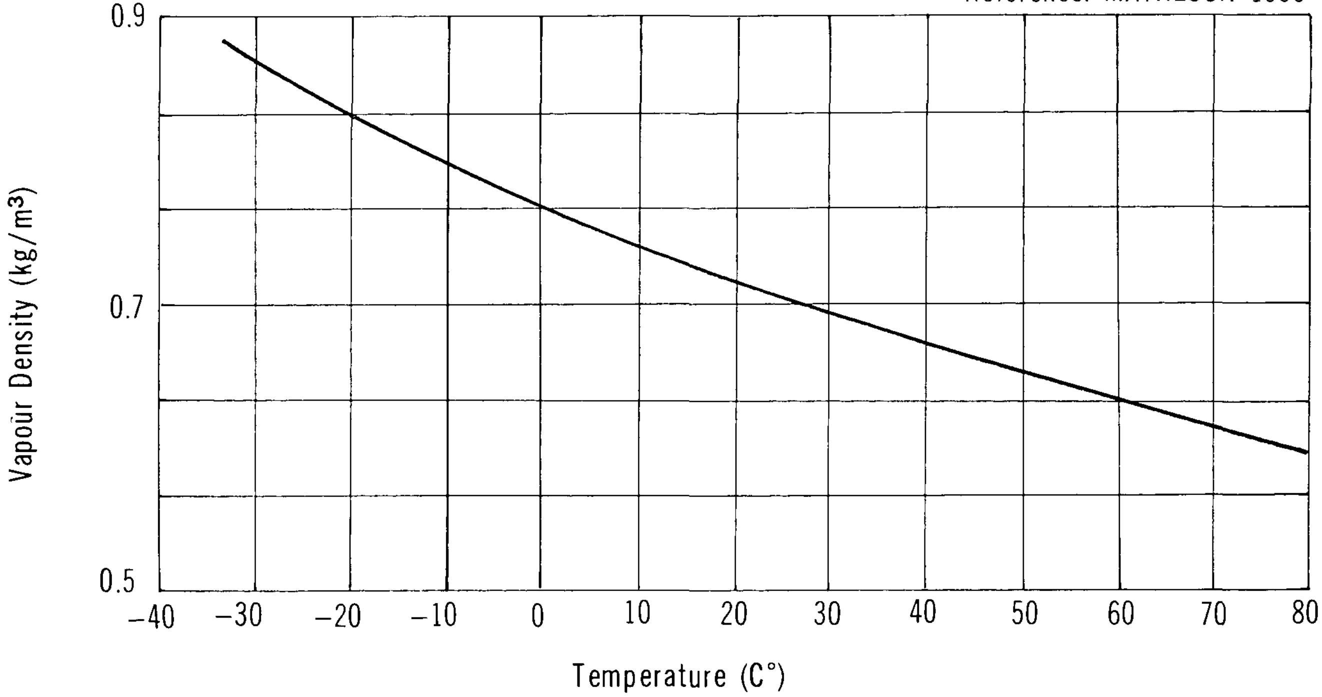


FIGURE 5

AMMONIA

VAPOUR PRESSURE VS TEMPERATURE

Reference: Chem. Eng. 1974

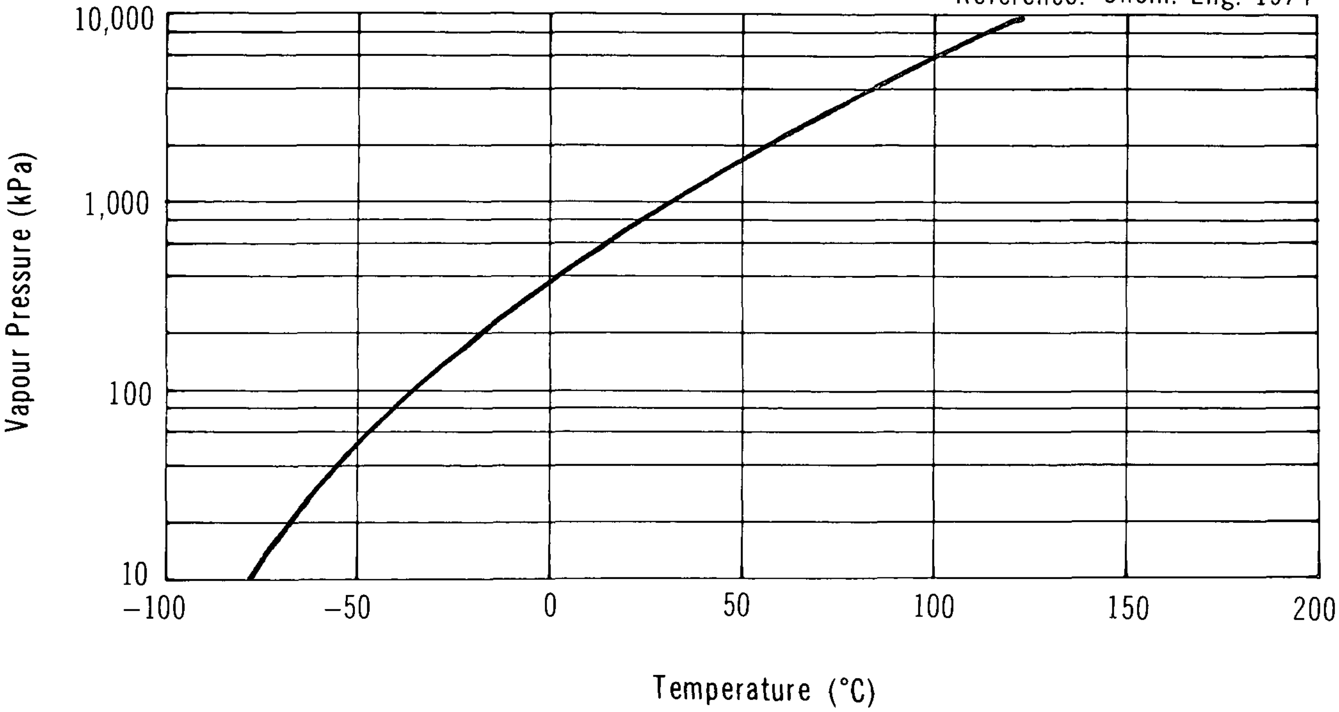


FIGURE 6

AMMONIA

LIQUID VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

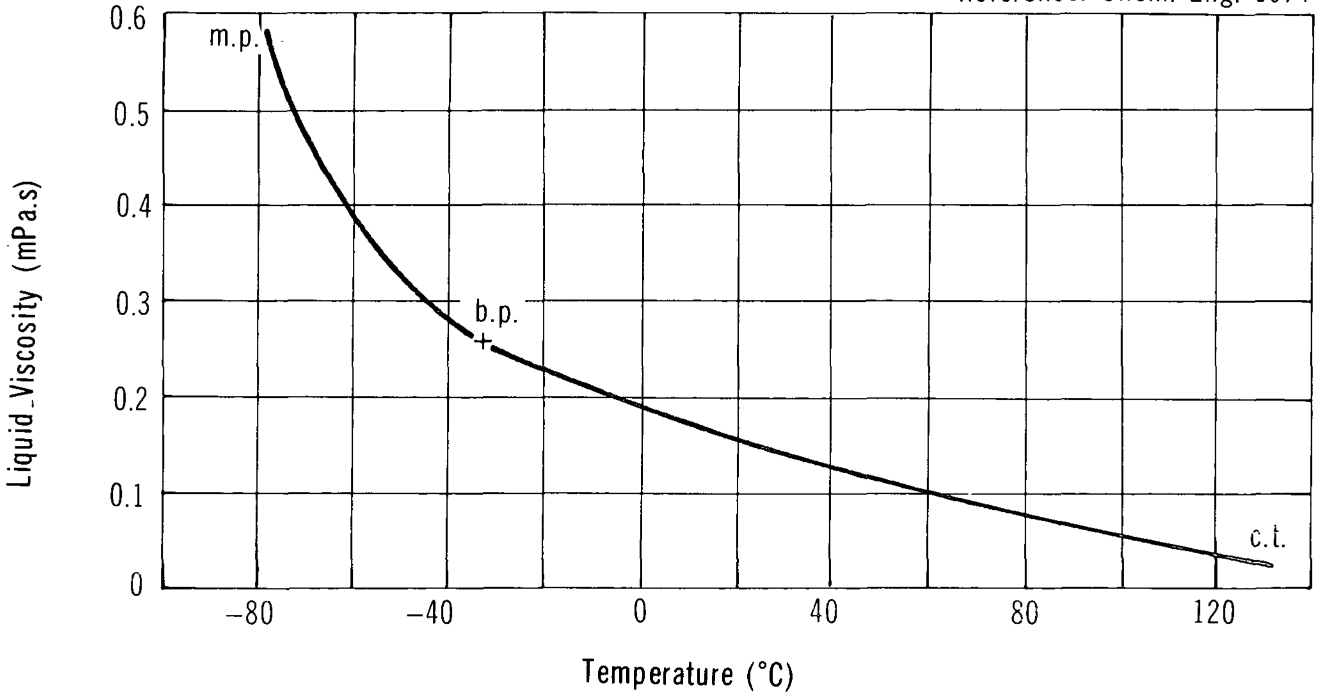


FIGURE 7

AMMONIA

VAPOUR VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

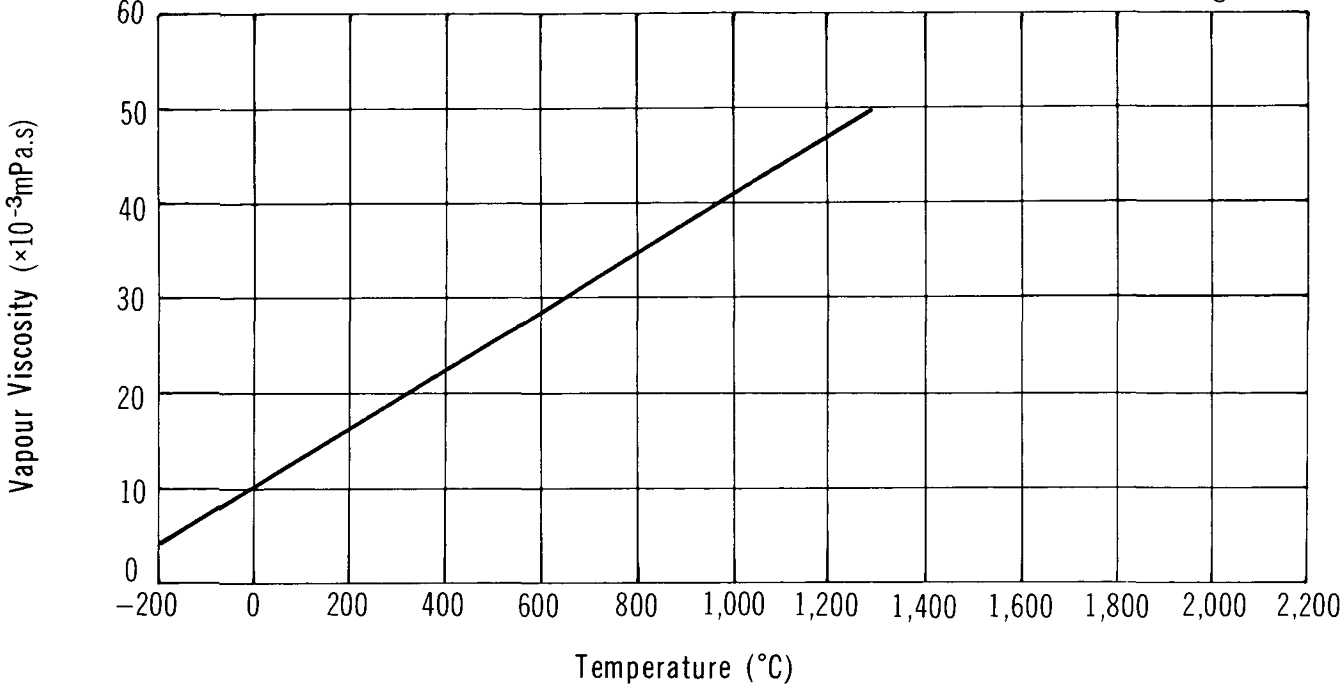
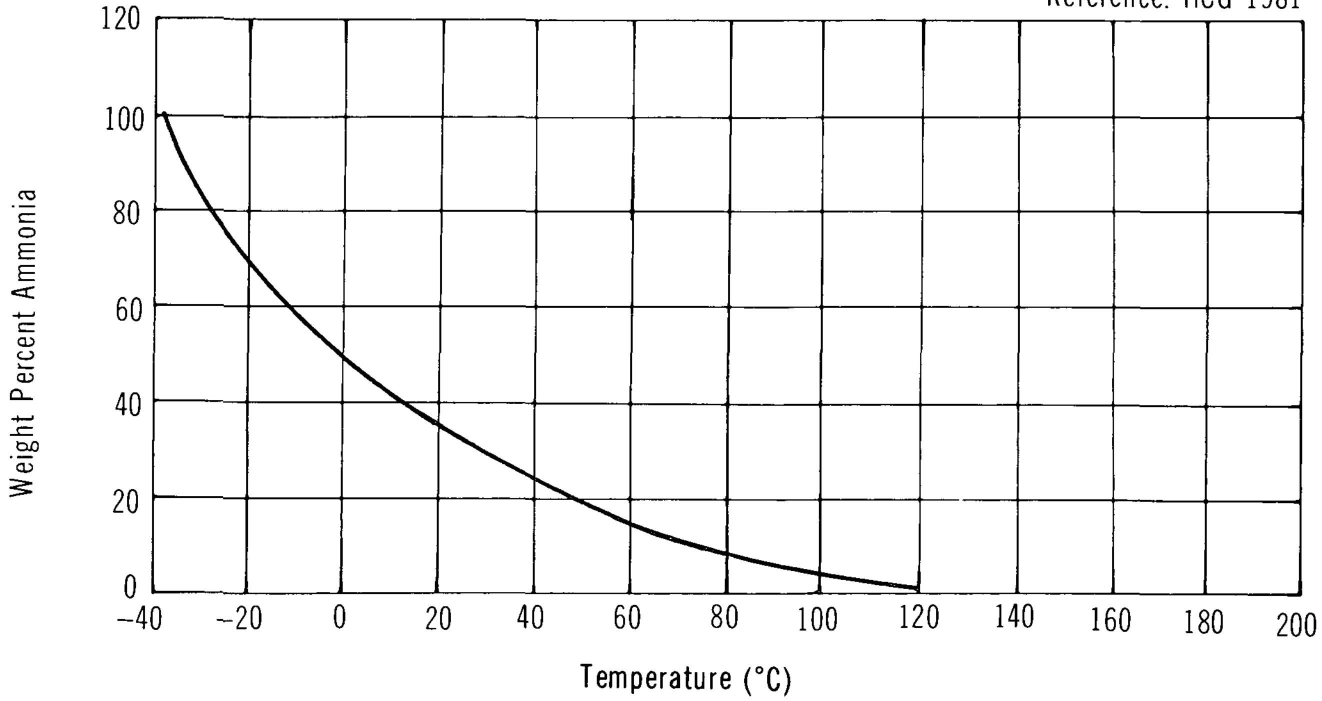


FIGURE 8

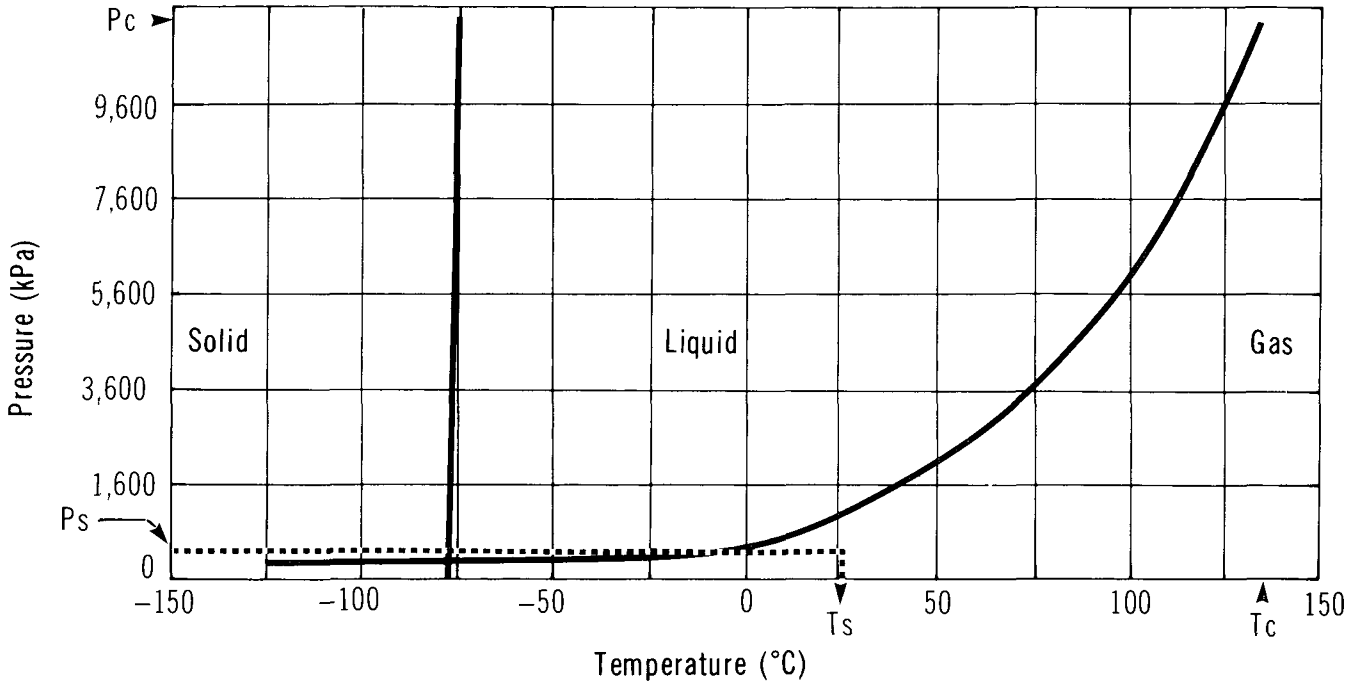
AMMONIA

SOLUBILITY IN WATER vs TEMPERATURE

Reference: HCG 1981



PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (GE 1979; Dow ERIS 1981)

3.1.1 Anhydrous. Anhydrous ammonia is sold in a number of grades: refrigeration, commercial, industrial, electronic and metallurgical, all of greater than 99.5 percent purity.

3.1.2 Aqueous Ammonia (Ammonium Hydroxide). Aqueous ammonia is available in technical and commercial grades, most commonly at 28 to 30 percent, with impurity levels below 0.5 percent. Dilute and concentrated solutions are not common.

3.2 Domestic Manufacturers (Corpus 1983; Scott 1979; CBG 1980)

These are corporate headquarters addresses and are not intended as spill response contacts.

Canadian Fertilizers Ltd.
P.O. Box 1300
Medicine Hat, Alberta
T1A 7N1
(403) 527-8887

C-I-L Inc.
45 Sheppard Avenue East
Willowdale, Ontario
M2N 2Z9
(416) 226-6110

Cominco Ltd.
200 Granville Street
Vancouver, British Columbia
V6C 2R2
(604) 682-0611

Cyanamid of Canada Ltd.
2255 Sheppard Avenue East
Willowdale, Ontario
M2J 4Y5
(416) 498-9405

Esso Chemical Canada
2300 Yonge Street
Toronto, Ontario
M5W 1K3
(416) 488-6600

Nitrochem Inc.
Suite 800
2055 Peel Street
Montreal, Quebec
H3A 1V4
(514) 849-9222

Sherritt Gordon Mines Ltd.
P.O. Box 28
Commerce Court West
Toronto, Ontario
M5L 1B1
(416) 363-9241

Simplot Chemical Co. Ltd.
P.O. Box 940
Brandon, Manitoba
R7A 6A1
(204) 728-5701

Western Co-operative Fertilizers Ltd.
11111 Barlow Trail S.E.
P.O. Box 2500
Calgary, Alberta
T2P 2X1
(403)279-4421

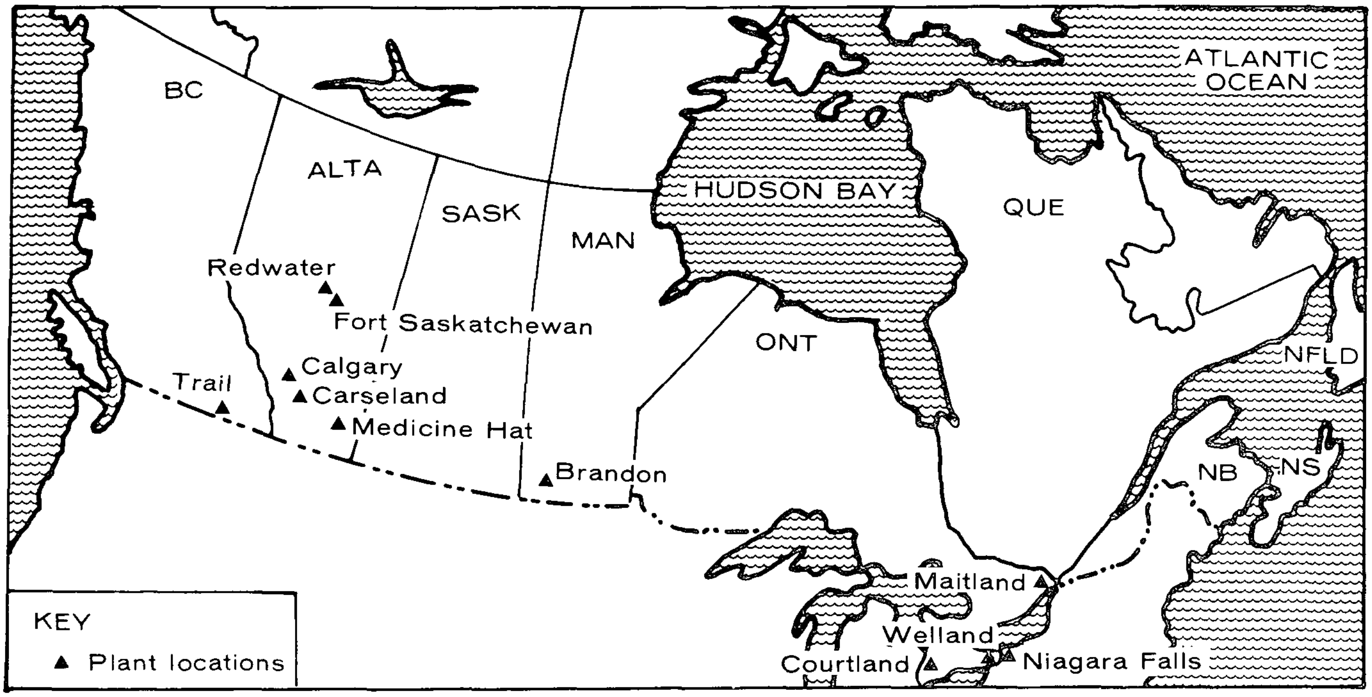
3.3 Major Transportation Routes

Current Canadian production of ammonia is located primarily in Alberta, at Calgary, Carseland, Medicine Hat and Fort Saskatchewan (67 percent of total production). Other production facilities are in Ontario, at Courtright, Maitland, and Niagara Falls (25.8 percent of total production); and in Manitoba and British Columbia. This is illustrated in Figure 10.

FIGURE 10

AMMONIA

CANADIAN PRODUCERS



A major market area for anhydrous ammonia is in Western Canada. The product is shipped either by rail tank car or by truck.

3.4 **Production Levels** (Corpus 1983)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
C-I-L, Courtright, Ont.	360
Canadian Fertilizers, Medicine Hat, Alta.	720
Cominco, Trail, B.C.	65
Cominco, Calgary, Alta.	107
Cominco, Carseland, Alta.	360
Cyanamid of Canada, Niagara Falls, Ont.	221
Esso Chemical Canada, Redwater, Alta.	225
Nitrochem, Maitland, Ont.	80
Sherritt Gordon Mines, Ft. Saskatchewan, Alta.	145
Simplot Chemical, Brandon, Man.	100
Western Co-operative Fertilizers, Medicine Hat, Alta.	60
Western Co-operative Fertilizers, Calgary, Alta.	60
TOTAL	2503
Domestic Production (1982)	2509
Imports (1982)	42
TOTAL SUPPLY	2551

3.5 **Future Development** (Corpus 1983)

A number of new ammonia plants came on-stream in 1983. Esso Chemical, in Redwater, Alberta, started a new plant with a capacity up to 544 kt/yr; the old plant was idled. Sherritt Gordon's Fort Saskatchewan plant was expanded, with an additional capacity of 340 kt/yr. C-I-L is expanding its Courtright plant by 373 kt/yr and is expected to be on-stream by late 1985.

3.6 Manufacture of Ammonia

3.6.1 General. Ammonia is manufactured in Canada by the high-pressure catalytic reforming of natural gas, followed by purification and then ammonia synthesis. The first two steps involve the generation of hydrogen gas, the introduction of nitrogen in the stoichiometric proportion, and the removal of carbon dioxide, carbon monoxide and water (catalytic poisons). The latter step involves the catalytic fixation of nitrogen at elevated temperatures and pressures and the recovery of ammonia.

3.6.2 Manufacturing Process. Conditions for the process vary greatly, but the chemistry of ammonia synthesis is basic to all commercial processes. In a typical process, natural gas feedstock is subjected to desulphurization, primary and secondary reforming, shift conversion, carbon dioxide removal, synthesis gas purification, and ammonia synthesis and recovery. The first step, desulphurization, is important because the nickel catalyst is susceptible to poisoning by sulphur. The most commonly used methods are adsorption by activated carbon at about 15-50°C or reaction with zinc oxide, or both. Hydrodesulphurization is sometimes recommended for organic sulphur compounds not easily removed by the former two agents. Other techniques include an absorption-stripping operation followed by zinc oxide treatment.

The natural gas feedstock is reformed by steam in two catalytic reaction stages. The first stage (primary) produces a partially reformed gas which is further processed in the secondary reformer to achieve the low methane content desired. The first operation is carried out in a furnace and the latter in a refractory-lined pressure vessel. The heat required is obtained by combustion using atmospheric oxygen to provide synthesis nitrogen. The reactions involved are shown below:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (\Delta H_{25°C} = 206.08 \text{ kJ/mole})$$

The reforming reaction is endothermic and considerable heat must be added to the process. The primary reformer catalyst is usually nickel supported on alumina. The reaction temperature is usually in the 750-850°C range at a pressure of about 2 860-3 550 kPa. The secondary reformer catalyst is nickel supported on alumina of very high thermal resistance.

The oxides of carbon contaminants, which deactivate the ammonia synthesizing catalyst, must be removed prior to that loop in the overall process. In this shift reaction, the carbon monoxide produced during reforming is converted to carbon dioxide and valuable hydrogen according to the equation:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (\Delta H_{25°C} = -41.17 \text{ kJ/mole})$$

The reaction is reversible, exothermic, and the equilibrium is favored by lower temperatures. The reaction velocity increases with temperature, however; as such, the bulk of the carbon monoxide is shifted to carbon dioxide in a high-temperature shift converter operating at 350-450°C. The gases are then cooled and the remaining carbon monoxide is converted to carbon dioxide (which is easier to remove) in a low-temperature converter. The high-temperature catalyst consists mainly of iron oxide (85 percent) and chromium oxide; copper oxide supported on zinc oxide and alumina is the catalyst in the low-temperature reaction.

The effluent gases from the shift converters contain about 17-19 percent (by volume) carbon dioxide. This is a poison for the ammonia synthesis catalyst and must be removed. This is accomplished first as a bulk process and then in a final purification step. Many processes are available. The choice of the specific carbon dioxide removal system depends on the overall plant design and the integration procedures required.

The next step is compression of the synthesis gas, usually to a range of 13 785-34 475 kPa. The compressed gas is then fed to the ammonia synthesis converter which generally falls into two classes, tubular or multiple bed. The feed gas is designed to maintain a 3:1 hydrogen to nitrogen ratio. The overall reversible reaction is shown below:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The reaction is carried out on a catalyst surface based on metallic iron (mainly magnetite) that has been promoted with other oxides. An increase in pressure increases the equilibrium percentage of ammonia as well as the reaction rate. A temperature increase accelerates the reaction, but decreases the equilibrium amount of ammonia and degrades the catalyst. The ammonia product is usually recovered by condensation; any unreacted feed gas is recycled through the synthesizer (Kirk-Othmer 1978).

3.7 **Major Uses in Canada** (Corpus 1983)

Ammonia is used in the production of urea, nitric acid, nylon, ammonium nitrate, nitrogen solutions, ammonium sulphate, ammonium phosphates, fertilizer mixes, hexamethylene diamine, ethanolamines, amines, nitriles, and other fertilizer usages. It is also used in the pulp and paper, mining, and refining industries.

In 1981, 82 percent of the total production was for domestic use, with 50 percent being used for fertilizer manufacture or directly as a fertilizer. The latter is becoming increasingly popular in Canada.

3.8 **Major Buyers in Canada** (Corpus 1983; CBG 1980)

Agricultural Chemicals, London, Ont.
Armak Chemicals, Saskatoon, Sask.
Cariboo Pulp & Paper, Quesnel, B.C.
Chinook Chemical, Sarnia, Ont.
CIP, Hawkesbury, Ont.
Dow Chemical of Canada, Sarnia, Ont.; Ft. Saskatchewan, Alta.
DuPont Canada, Maitland, Ont.
Fraser, Atholville, N.B.
Inco Metals, Copper Cliff, Ont.
Nitrochem, Maitland, Ont.
Tembec Industries, Temiskaming, Que.

Union Carbide Canada, Montreal, Que.
United Co-operatives of Ont., Mississauga, Ont.
Western Forest Products, Port Alice, B.C.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Bulk shipment of anhydrous ammonia and solutions of ammonia is primarily by railway tank cars and tank motor vehicles. Some anhydrous ammonia is transported in cylinders and some solutions can be shipped in drums, carboys and bottles.

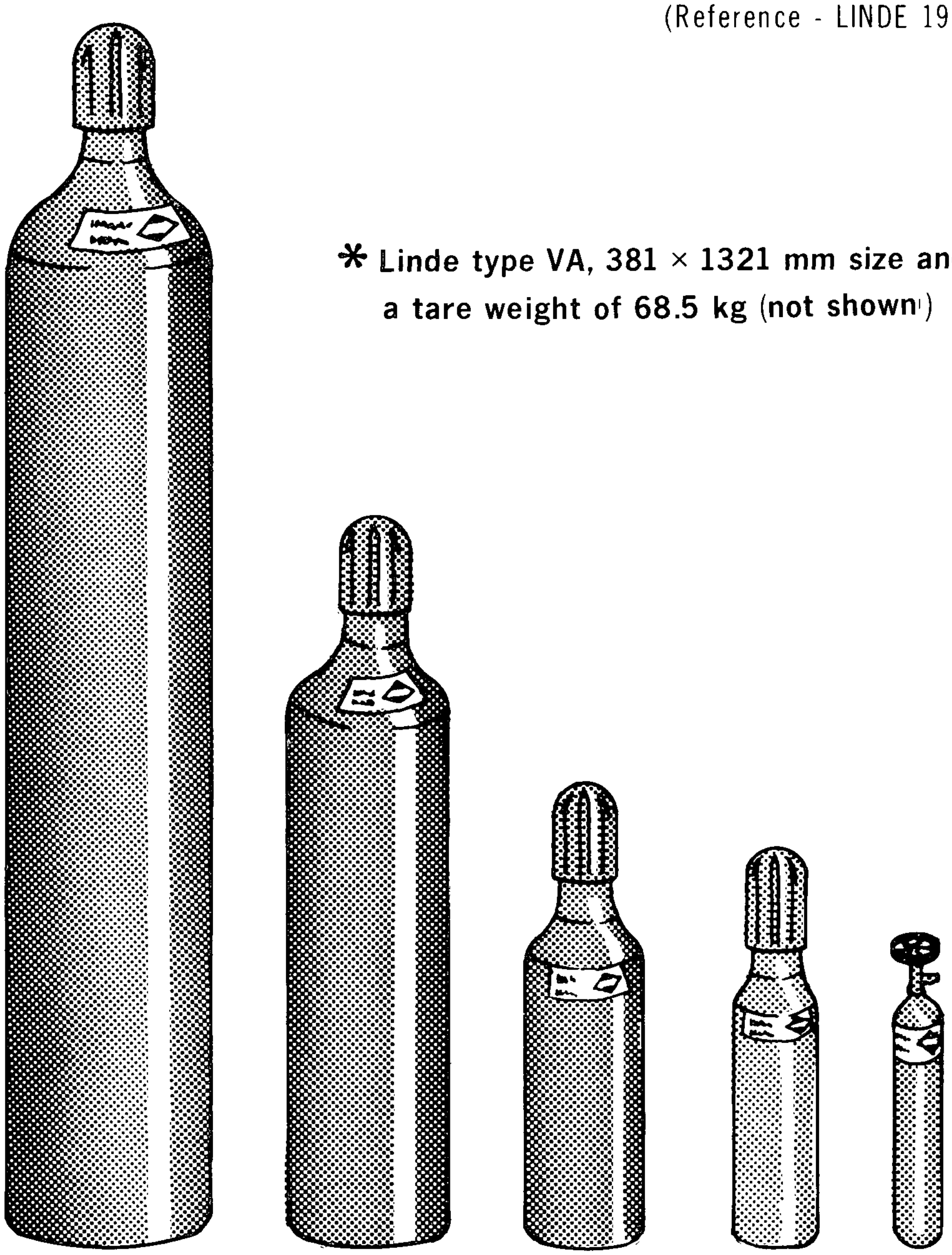
4.1.1.1 Cylinders. Anhydrous ammonia cylinders are of seamless or welded steel construction, with tare weights ranging from 1.8 kg (4 lb.) to 86 kg (190 lb.) (Matheson 1980; Linde 1981) An 86 kg (190 lb.) cylinder has a gross weight of 154 kg (340 lb.), a diameter of 260 mm (10 in.) and a length of 1400 mm (55 in.). Cylinders must comply with CTC/DOT specifications 3A480, 3AA480, 3A480X, 3E1800, 4A480 and 4AA480 (RTDCR 1974). Each specification is described in Table 2; common cylinders are shown in Figure 11. Ton containers are rarely used in Canada.

TABLE 2 CYLINDER SPECIFICATIONS

CTC/DOT* Specification Number	Description
3A480	Seamless steel cylinder. Steel, open hearth or electric, of uniform quality, carbon content not over 0.55 percent, phosphorus not over 0.045 percent and sulphur not over 0.050 percent. Service pressure 3312 kPa (480 psi).
3AA480	Seamless steel cylinder. Maximum carbon content 0.28 percent. Steel, open hearth or electric, of uniform quality. Service pressure 3312 kPa (480 psi).
3A480X	Seamless steel cylinder. Carbon content 0.4 percent (maximum). Service pressure 3312 kPa (480 psi).
3E1800	Seamless steel prescribed as in 3A480. Service pressure 12 411 kPa (1800 psi).
4A480	Forge-welded steel cylinder. Service pressure 3312 kPa (480 psi).

COMMON GAS CYLINDERS*

(Reference - LINDE 1981)



* Linde type VA, 381 × 1321 mm size and a tare weight of 68.5 kg (not shown)

Industry designation		K	Q	G	F	LB
Approx. size	(mm)	229×1320	178×787	152×508	102×432	51×330
	(in)	9×52	7×31	6×20	4×17	2×13
Approx. weight (empty)	(kg)	60	29	13	5	1
	(lb)	132	65	29	10	4

TABLE 2 CYLINDER SPECIFICATIONS (Cont'd)

CTC/DOT* Specification Number	Description
4AA480	Welded steel cylinder. Service pressure 3312 kPa (480 psi).

* Canadian Transport Commission and Department of Transportation (U.S.)

4.1.1.2 Railway tank cars. Railway tank cars used for ammonia solutions and anhydrous ammonia differ substantially in that the solutions are regulated as corrosive liquids while the anhydrous form is regulated as a compressed gas under pressure. Pressure vessels used to transport anhydrous ammonia or ammonia solutions containing more than 44 percent ammonia will be discussed first; ammonia solution tankers will be dealt with later.

Usually constructed of carbon or stainless steel, railway tank cars are designed to transport anhydrous ammonia in capacities of 16 to 90 tonnes. Cars must comply with CTC/DOT specifications described in Table 3 (RTDCR 1974).

A typical 105A300W railway tank car is illustrated in Figure 12; Table 4 indicates railway tank car details associated with this drawing (TCM 1979).

Five valves are mounted inside the dome cover in an arrangement similar to that used for chlorine tank cars. Four of these are angle valves; the fifth, mounted in the center, is a safety relief valve. A gauging device, 18 mm (3/4 in.) thermometer, and 6 mm (1/4 in.) testing tube may replace one of the angle valves on some cars.

Under each 51 mm (2 in.) liquid valve is a 76 mm (3 in.) eduction pipe fastened to the manway cover and extending to the bottom of the tank. At the top of each eduction pipe, immediately below the manway cover, is a 76 mm (3 in.) rising-ball, excess-flow valve (AA 1970) designed to close when the rate of flow of liquid anhydrous ammonia exceeds about 3180 kg/h (1000 gal./h). This is a protective device designed to close automatically against the flow of liquid anhydrous ammonia if the angle valve is broken off or, under certain conditions, if the unloading line is severed. A similar valve is installed below the gas valve.

Ammonia solutions are transported in railway tank cars described in Table 5 (RTDCR 1974). Such tanks may be unloaded through the bottom outlet, if permitted, or may be pumped from the dome outlet.

TABLE 3 RAILWAY TANK CAR SPECIFICATIONS FOR ANHYDROUS AMMONIA

CTC/DOT* Specification Number	Description
105A300W	Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Safety valve (1550 kPa) (225 psi). Bottom outlet or washout prohibited.
106A500	Multiple unit car with removable steel forge-welded uninsulated ton containers mounted on underframe. Safety valve (2590 kPa) (375 psi).
106A500X	Same as 106A500 except tank has fusion-welded longitudinal seams and forge-welded head seams.
112A340W	Steel fusion-welded tank with manway nozzle. Uninsulated. Light-reflective paint. Top unloading arrangement required. Safety valve (1760 kPa) (225 psi). Bottom outlet or washout prohibited.
112A400W	Same as 112A340W except safety valve set at 2070 kPa (300 psi).
114A340W	Steel fusion-welded tank with manway nozzle. Uninsulated. Light-reflective paint. Manway location optional. Safety valve (1760 kPa) (225 psi). Bottom outlet and washout optional.

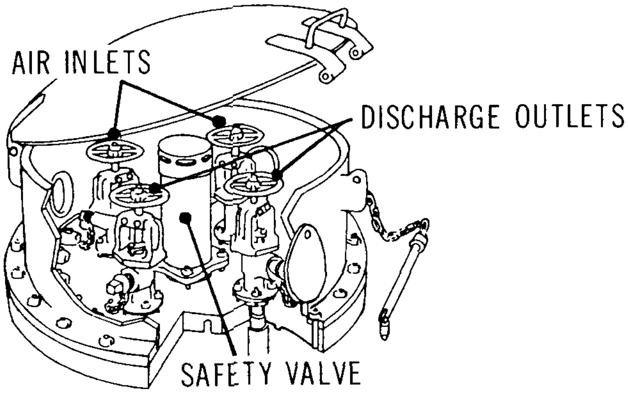
* Canadian Transport Commission and Department of Transportation (U.S.)

4.1.1.3 Tank motor vehicles. Anhydrous ammonia tank motor vehicles consist of a cargo tank pulled by a tractor. The maximum tank capacity is restricted by highway load limits. They must comply with DOT specifications TC331 or MC331 as outlined in Table 6 (TDGC 1980). Most tanks have a capacity of 16 tonnes, but the capacity varies from 15 to 20 tonnes.

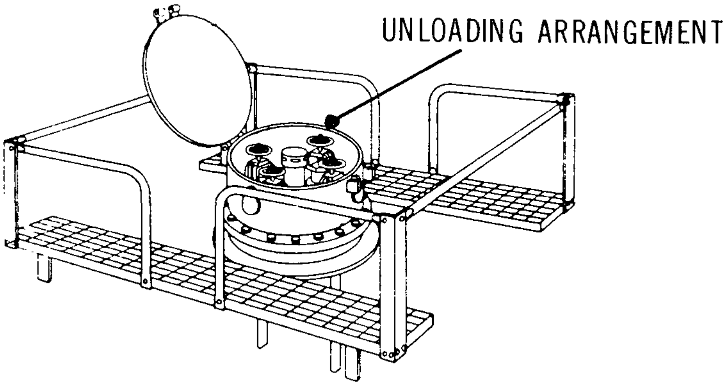
All tanks are provided with 100 mm (4 in.) of insulation protected by a steel jacket. The only tank opening permitted is a manway located at the top. The valve

RAILWAY TANK CAR - CLASS 105A300W

Reference: TCM 1979; RTDCR 1974



Detail of top unloading arrangement



Detail of loading platform

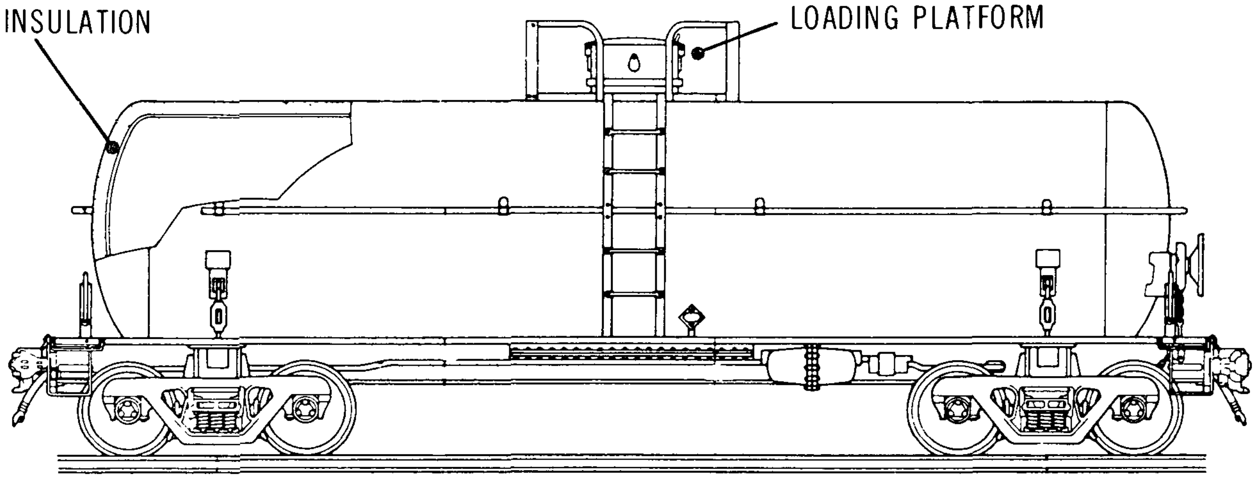


Illustration of tank car layout

TABLE 4 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A300W (TCM 1979; RTDCR 1974)

	Tank Car Size (Imp. Gal.)		
Description	9000	21 000	28 000
Overall			
Nominal capacity	41 000 L (9000 gal.)	95 000 L (21 000 gal.)	127 000 L (28 000 gal.)
Car weight - empty	30 300 kg (66 800 lb.)	40 800 kg (90 000 lb.)	50 800 kg (112 000 lb.)
Car weight - (max.)	80 300 kg (177 000 lb.)	83 500 kg (184 000 lb.)	119 000 kg (263 000 lb.)
Tank			
Material	Steel	Steel	Steel
Thickness	17.5 mm (11/16 in.)	17.5 mm (11/16 in.)	17.5 mm (11/16 in.)
Inside diameter	2.2 m (88 in.)	2.4 m (95 in.)	3.0 m (120 in.)
Test pressure	2070 kPa (300 psi)	2070 kPa (300 psi)	2070 kPa (300 psi)
Burst pressure	51 700 kPa (750 psi)	51 700 kPa (750 psi)	51 700 kPa (750 psi)
Approximate Dimensions			
Coupled length	13 m (42 ft.)	20 m (65 ft.)	20 m (67 ft.)
Length over strikers	12 m (40 ft.)	19 m (63 ft.)	20 m (64 ft.)
Length of truck centers	9 m (29 ft.)	16 m (52 ft.)	16 m (53 ft.)
Height to top of grating	4 m (12 ft.)	4 m (12 ft.)	4 m (12 ft.)
Overall height	5 m (15 ft.)	5 m (15 ft.)	5 m (15 ft.)
Overall width	3.2 m (127 in.)	3.2 m (127 in.)	3.2 m (127 in.)
Length of grating	2-3 m (7-10 ft.)	2-3 m (7-10 ft.)	2-3 m (7-10 ft.)
Width of grating	1.5-2 m (5-6 ft.)	1.5-2 m (5-6 ft.)	1.5-2 m (5-6 ft.)
Loading/Unloading Fixtures			
Unloading Connection	25 mm (1 in.) via valve and 32 mm (1 1/4 in.) check valve		
Valving	2 unloading connections and 2 valves to vapour space		
Safety Devices	Safety relief valve set at 1550 kPa (225 psi)		
Insulation	102 mm (4 in.) foam or cork insulation		

TABLE 5 RAILWAY TANK CAR SPECIFICATIONS FOR AMMONIA SOLUTIONS

CTC/DOT* Specification Number	Description
105A100W	Steel fusion-welded tank with dome. 2 percent dome. Insulation required. Safety relief valve (517 kPa) (75 psi). Bottom outlet or washout prohibited.
105A100ALW	Same as 105A100W except with aluminum alloy.
109A100ALW	Aluminum alloy tank with dome. Insulation optional. Safety relief valve (517 kPa) (75 psi).
109A300W	Steel tank with dome. Insulation optional. Safety relief valve (1550 kPa) (225 psi). Bottom washout optional. Bottom outlet prohibited.
111A100W4	Steel tank without dome. Insulation required. Safety relief valve (517 kPa) (75 psi). Bottom outlet and washout prohibited.

* Canadian Transport Commission and Department of Transportation (U.S.)

TABLE 6 TANK MOTOR VEHICLE SPECIFICATIONS

Transport Canada Specification Number	Description
TC331 (or MC331)	Seamless or welded steel tank. Design and construct in accordance with ASME Code. One opening with protective housing and manway cover. Maximum design pressure 3450 kPa (500 psi). Postweld heat treatment as per ASME Code. Gauging device.

arrangement is the same as that on tank cars. The minimum design pressure of the tank is 1825 kPa (265 psi) (TDGC 1980).

Ammonia solutions are transported in tank trucks similar to their railway tank car counterpart.

4.1.2 Packaging. Ammonia solutions are commonly packaged in drums constructed of a variety of materials, as described in Table 7 (TDGC 1980). Also, 50 L maximum (41 kg) carboys and 1 L maximum capacity glass bottles packed in wooden cases are used.

TABLE 7 DRUMS

Type of Drum	Designation	Description	Figure No. (If Any)
Steel	1A1	Nonremovable head, reusable	13
	1A1A	1A1 with reinforced chime	13
	1A1B	1A1 with welded closure flange	13
	1A1C	1A1 with lead coating	13
	1A1D	1A1 with coating (other than lead)	13
	1A2	Removable head, reusable	13
	1A3	Nonremovable head, single use only	13
Plastic	1H1	Nonremovable head. Maximum capacity 250 L (55 gal.). Maximum net mass 400 kg (882 lb.).	
Steel drums with inner plastic receptacles	6HA1	Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity of 225 L (49 gal.).	

* See Section 4.3 of this report.

4.2 Off-loading

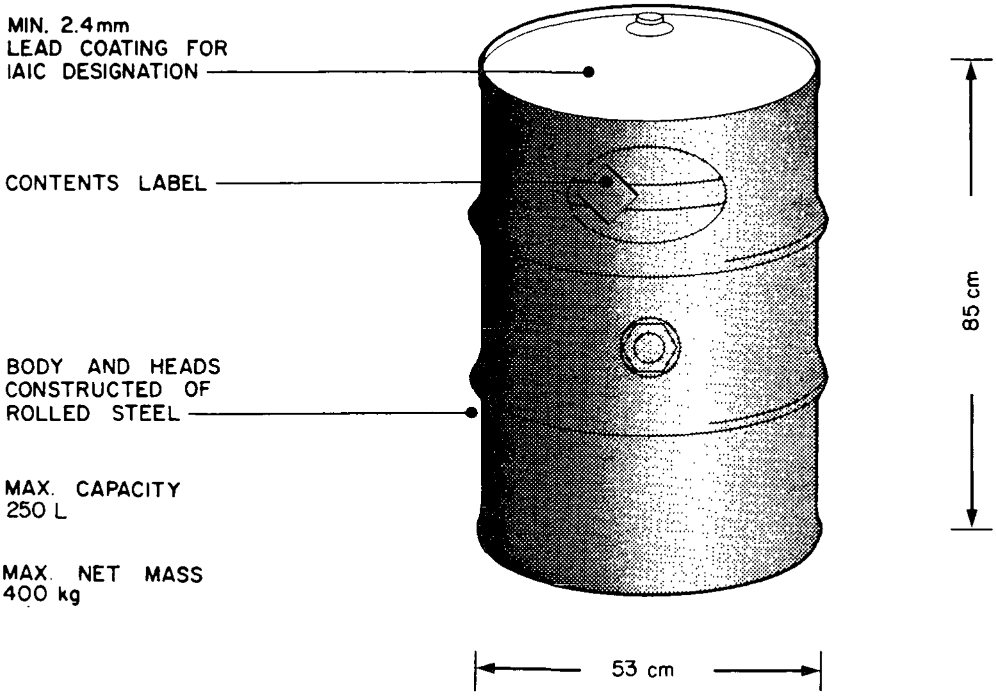
4.2.1 Off-loading Equipment and Procedures for Cylinders. Both cylinders and ton containers are handled and stored in the same manner. The following points should be observed when handling and storing containers:

- Valve protection hoods should be in place (MCA 1960).
- Containers should not be stored near ventilating systems.
- Store to minimize external corrosion.
- Store cylinders upright, ton containers on their sides.
- Store full and empty containers separately.

A flexible hose connection between the container and the piping system should be used.

TYPICAL DRUM CONTAINER

Typical steel drum



Cylinders and containers should be placed in a vertical or horizontal position as previously described to deliver anhydrous ammonia gas or liquid, respectively.

4.2.2 Off-loading Equipment and Procedures for Railway Tank Cars and Tank Motor Vehicles. Railway tank cars and tank motor vehicles are basically off-loaded in the same manner but only after the following precautionary steps have been undertaken:

- Unloading operations to be performed only by properly instructed personnel.
- Dead-end siding used only for ammonia rail cars to be provided.
- Brakes must be set, wheels chocked and a proper derail employed (MCA 1960).
- Suitable operating platform to be provided at unloading point.

The anhydrous ammonia railway tank car or highway vehicle is unloaded by compressor (MCA 1960) while the ammonia solution tanker is unloaded by gravity or pump (MCA 1947).

When using the compressor, anhydrous ammonia liquid is discharged from one of the two liquid angle valves by creating a pressure differential between the tank car and the storage tank. The suction side of the compressor is connected to the top of the storage tank; the discharge side is connected to a liquid angle valve (MCA 1960).

When all the liquid has been removed from the tanker, the compressor suction and discharge may be reversed to recover the anhydrous ammonia gas in the car until the tank pressure is about 35 kPa (5 psi) (MCA 1947).

The ammonia solution tanker is unloaded by pump from a top discharge valve, or by gravity or pump through the bottom discharge outlet, usually a 51 mm (2 in.) connection.

4.2.3 Specifications and Materials for Off-loading Equipment. Piping for ammonia service is usually Schedule 40 seamless black iron or carbon steel (HCG 1981). Use extra heavy steel when threaded joints are used. Pipeline joints should preferably be flanged or welded. Forged steel tongue-and-groove ammonia flanges should be used.

Flexible connectors should be installed between tankers and rigid piping systems. For ammonia solutions, a rubber hose, suitable for 860 kPa steam service equipped with suitable union type couplings for ammonia service, is recommended. For anhydrous ammonia, use special hose equipped with high-pressure screw fittings.

Standard steel valves are in common use for ammonia service (CCPA 1982). Diaphragm valves made from cast steel and lined with polyvinylidene fluoride are also recommended for ammonia service (Dow PPS 1972).

4.3 Compatibility of Ammonia with Materials of Construction

The compatibility of ammonia with materials of construction is indicated in Table 8. The unbracketed abbreviations are described in Table 9. The rating system for this report is briefly described below.

Recommended:	This material will perform satisfactorily in the given application.
Conditional:	Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.
Not Recommended:	Material will be severely affected in this application and should not be used.

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	10%	121	Chlorinated Polyether (DCRG 1972)		
	10%	107	PP (DCRG 1972)		
	10%	93	PVDF (DCRG 1972)		
	10%				PVDC (DCRG 1972)
	10%	To operating limit of material	PVC I ABS PE (MWPP 1978)		
	Gas	107	Chlorinated Polyether PP (DCRG 1972)		
	Gas, Dry	23	PE (DPPED 1967)		
	Gas, Dry	49			PE (DPPED 1967)
	Gas, Dry	23			ABS (DPPED 1967)
	Gas, Dry	60	PVC I PVC II (DPPED 1967)		

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (cont'd)	Gas	24	ABS* (MWPP 1978)		
	Gas	To operating limit of material	PVC I PE* (MWPP 1978)		
	Anhydrous	107	Chlorinated Polyether PP (DCRG 1972)		
	Anhydrous	135	PVDF (DCRG 1972)		
	Liquid	23	Mild Steel (CCPA 1982)		PVC I (DPPED 1967)
2. Valves	Gas	21	SS 316 (JSSV 1979)		
	All-Liquor	Boiling	Mild Steel (CCPA 1982) SS 316 (JSSV (1979)		Copper, Copper Alloys (CCPA 1982)
	Water	Boiling	SS 316 (JSSV 1979)		
3. Pumps	Solutions		All Iron (HIS 1969)		
4. Others	Gas 100%	60	PE, PP POM, NR NBR, IIR EPDM, CR CSM (GF)		uPVC FPM (GF)
	Gas	Cold	SS 302 SS 304 SS 316 SS 430 (ASS) NR, SBR CR, NBR IIR, CSM EPDM (GPP)		
	Gas	Hot			SS 302 SS 304 SS 316 SS 430 (ASS)

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
4. Others (cont'd)	Gas	Hot			NR, SBR CR, NBR IIR EPDM (GPP)
	Anhydrous		NR SBR CR IIR EPDM (GPP)		NBR CSM (GPP)
	Anhydrous	20	SS 302 SS 304 SS 316 SS 430 (ASS)		Copper Copper Alloys (CCPA 1982)
	Liquified	20	PE, PP		uPVC FPM (GF)
		(100%)	POM, NR NBR, IIR EPDM, CR CSM (GF)		
	10%	60	PVC (TPS 1978)		
	10%	66	PP (TPS 1978)		
	10%	85	PVC (TPS (1978)		
	10 to 30%	24 to 100	Glass (CDS 1967)		
	10 to 30%	24	Concrete (CDS 1967)		
	100%	24			Wood (CDS 1967)

* This material has been given a lower rating in a similar application by another reference.

TABLE 9 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Aluminum
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
	Chlorinated Polyether
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Concrete
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
	Iron
IIR	Isobutylene/Isoprene (Butyl)
NBR	Acrylonitrile/Butadiene Rubber (Nitrile, Buna N)
NR	Natural Rubber
	Nickel
	Nickel-Copper Alloy (Monel)
	Nickel-Molybdenum (Hastelloy Alloy C)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (followed by grade)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SS (followed by grade)	Stainless Steel
SBR	Styrene-Butadiene (GR-S, Buna S)
uPVC	Unplasticized Polyvinyl Chloride
	Wood

5 CONTAMINANT TRANSPORT

5.1 General Summary

When anhydrous ammonia is spilled, it will form a liquid pool, spreading on the surface of a water body or on the ground. Initially, vapour will be rapidly released in the from of a "puff". The evaporation process will cool the spilled liquid and thus slow the vapour release rate after the initial puff.

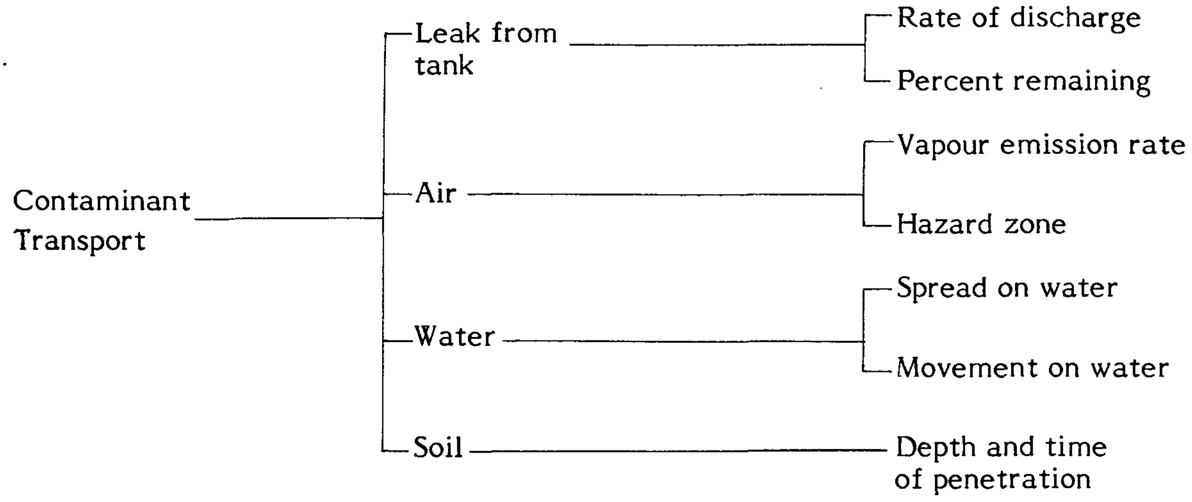
Ammonia dispersion in air has been the topic of a number of studies. Observations of actual and experimental spills have confirmed that ammonia gas behaves initially like a heavy gas despite its apparent 0.6 specific gravity in air. This is attributed to the formation of aerosols. Recent experiments by the Lawrence Livermore Laboratories have shown that this aerosol behaviour can result in concentrations of up to 9 times that predicted at a distance 3 km downwind. The "heavy gas" effect is known to increase with increasing spill size. It is currently believed that ammonia will initially behave as a heavy gas (as an aerosol) for up to 1 hour for a large spill and very stable atmospheric conditions. For small spills (about 1 tonne) and more unstable atmospheric conditions, the heavy gas behaviour would last for only about 10 minutes. The gas dispersion model presented in this manual correlates closely with recent experimental results and thus takes into account the aerosol behaviour.

Anhydrous ammonia is modelled throughout this section as it represents the worst case. Solutions will release significantly less vapour into the air. Modelling in soil and water can be accomplished by taking the spill volume as the percentage times the total volume.

When spilled on water, some of the ammonia will vaporize; the rest will dissolve in the water body. An experimental program has shown that when liquid ammonia is spilled onto water, about 70 percent of the material enters the water phase to form an aqueous ammonia solution. The results seemed to be independent of spill size (sizes ranged from 2500 cm^3 through 0.02 m^3 to 0.19 m^3), method of spill (instantaneous versus a controlled rate), and water temperature, salinity or depth. Under these specific test conditions, visual observations and vapour cloud data indicated that the ammonia vapour was less dense than the ambient air and the plume rose while moving downwind. The density of saturated ammonia vapour at 101 kPa is about 0.89 kg/m^3, whereas for air at 27°C, the density is near 1.2 kg/m^3. It should be noted, however, that the dynamics of an accidental spill of a large amount of anhydrous liquid ammonia onto water may play a significant role in determining the fraction of the spilled liquid that is ultimately released to the atmosphere. For example, an instantaneous release of liquid ammonia onto the water surface results in violent boiling of the ammonia. This may cause aerosols of liquid ammonia to be generated and released to the atmosphere. In such a case, the effective partition coefficient (percent retained in the water) will be smaller than that predicted by the thermodynamic analysis generated by the study (Raj 1978).

Liquid ammonia spilled onto a soil surface will vaporize to some degree; it may also adsorb onto the soil at a rate dependent on the soil type and its degree of saturation with water (see Section 6.7). As mentioned above, the spilled liquid will flow along the contours of the ground, form pools and boil vigorously. The rate of vaporization will decrease as the temperature of the pooled liquid and the underlying ground decreases. Water spray and/or dilution water directed onto the pooled liquid will cause violent boiling until the ammonia is diluted sufficiently such that an aqueous ammonia solution is afforded.

The following factors are considered for the transport of spilled material in the air, water and soil media:



5.2 Leak Nomograms

5.2.1 Introduction. Ammonia is commonly transported as a liquified compressed gas at ambient temperature. While the capacities of the railway tank cars vary widely, one size has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L.

If a tank car loaded with liquified ammonia is punctured on the bottom, all of the contents will drain out. The instantaneous discharge rate (q) is a function of the height of the fluid above the hole (H), the internal pressure of the tank (P), the hole size

(A) and shape, and a coefficient of discharge (C_d). For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

If the tank car is punctured in the top or at any point above the liquid level, gas will be vented until all of the liquid has vaporized and the internal and external tank pressures have equalized. For the purposes of nomogram preparation, the liquid is assumed to remain at a constant temperature (isothermal) equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid is vaporized. The venting rate is a function of the internal tank pressure (P), which is equal to the saturated vapour pressure (P_{sat}) of the liquid at temperature T. The assumed maximum tank ambient temperature is 40°C, yielding a saturated vapour pressure (P_{sat}) of 1600 kPa.

The assumption of isothermal conditions will maximize the gas release rate from the tank and will be a worst case situation for most accidents. A puncture will release gas at a rate initially as predicted below; however, the evaporative cooling will reduce the vapour pressure and subsequently the emission rate. Under some conditions, the liquid may cool to or below its boiling point, diminishing the vapour emission by orders of magnitude. Depending on circumstances, water ice may also form at the puncture site or at the liquid surface, further slowing the vapour release.

The following approximations may be made with regard to vapour release rates/conditions:

a) Isothermal conditions may be assumed when the container is involved in a fire and part of the insulation is gone.

b) The vapour release rate may be one order of magnitude slower than that afforded by condition (a) above with a high ambient air temperature and part of the insulation gone.

c) The vapour release rate may be two to three orders of magnitude slower than that afforded by condition (a) above with a relatively cool ambient air temperature and varying degrees of insulation removed.

d) The vapour release rate may be four to seven orders of magnitude slower than that afforded by condition (a) above with a relatively cool ambient air temperature and little insulation lost.

Catastrophic damage may result in loss of the entire contents of the car to the environment, resulting in the instantaneous formation of a massive vapour cloud (puff) comprised of a percentage of the total liquid mass released that will be dependent on the overall environmental conditions.

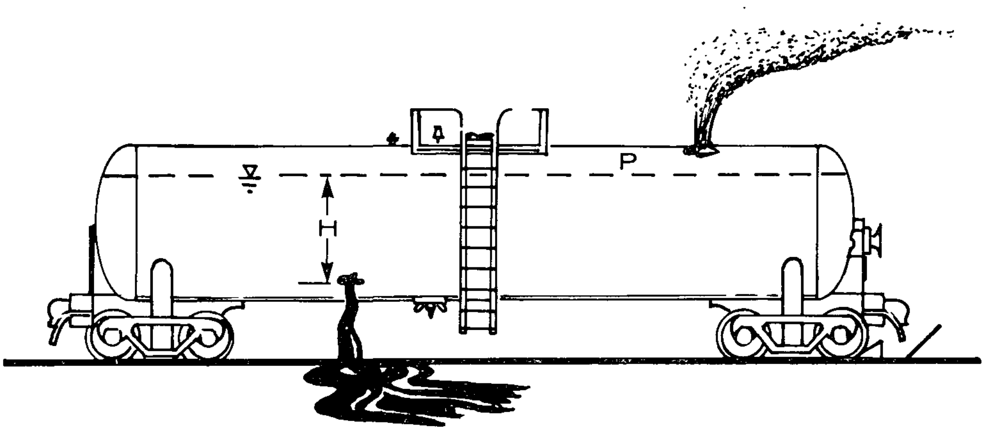


FIGURE 14 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

The aim of the nomograms is to provide a simple means to obtain the time history of the venting process. This may include venting from a bottom puncture (liquid release) or from a puncture above the liquid level (gas venting). The details of the models used to calculate venting rates are described in the Introduction Manual.

5.2.2 Nomograms.

5.2.2.1 Bottom puncture - liquid venting.

Figure 15: Percent remaining versus time. Figure 15 provides a means of estimating the percent of ammonia remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car (2.75 m ϕ x 13.4 m long) is assumed to be initially full (at t=0) with a volume of about 80 000 L of ammonia at 40°C. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

Figure 16: Discharge rate versus puncture size. Figure 16 provides a means of estimating the maximum discharge rate (L/s) for a number of equivalent hole diameters. As the pressure force dominates the gravitational force, the discharge rate remains relatively constant as the tank empties.

FIGURE 15

AMMONIA (Anhydrous)

PERCENT REMAINING vs TIME

Puncture in Bottom of Tankcar

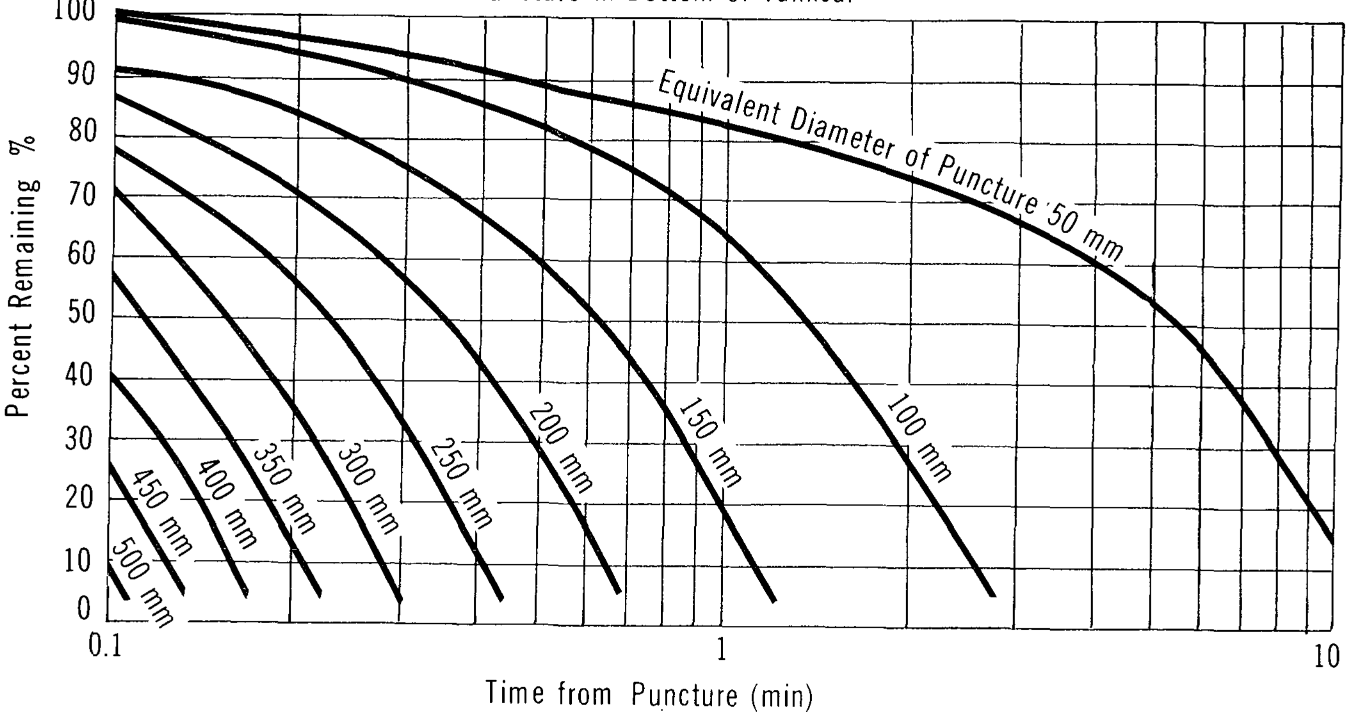
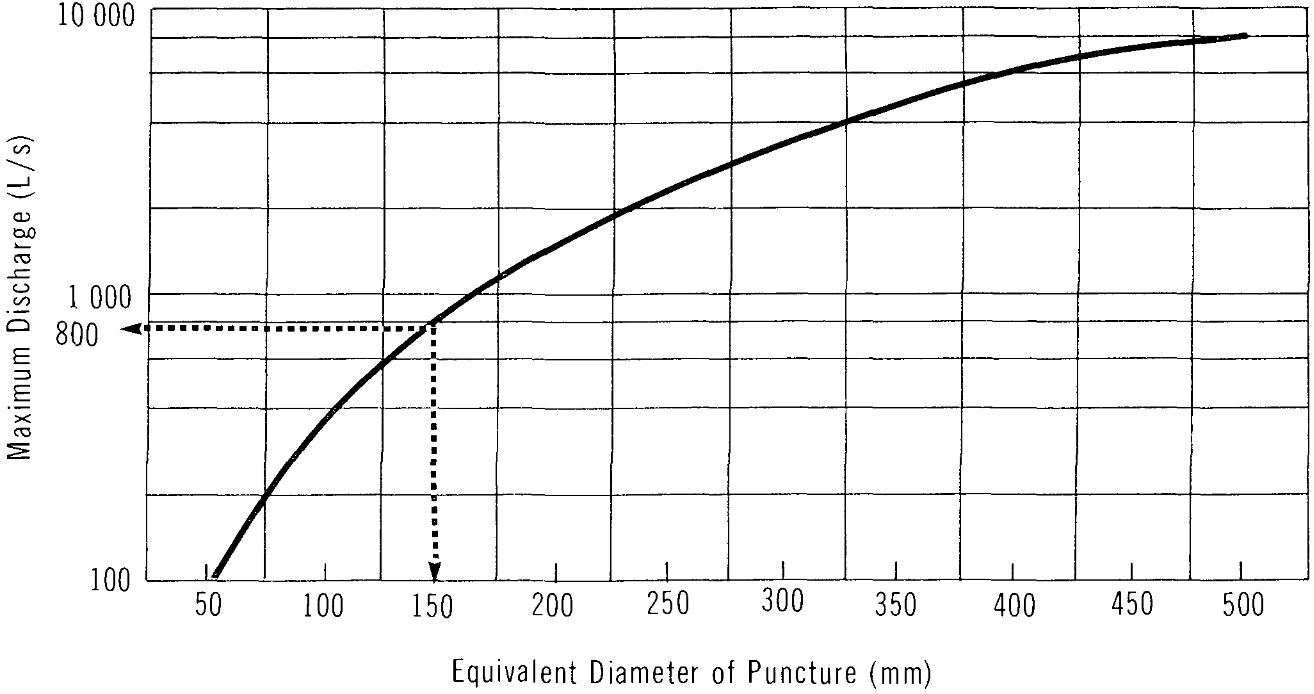


FIGURE 16

AMMONIA (Anhydrous)

DISCHARGE RATE vs PUNCTURE SIZE

Puncture in Bottom of Tankcar



5.2.2.2 Top puncture - gas venting.

Figure 17: Percent remaining versus time. Figure 17 provides a means of estimating the percent of ammonia remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture. As isothermal conditions have been assumed, the internal pressure and venting rate are constant.

Figure 18: Discharge rate versus puncture size. Figure 18 presents the relationship between discharge rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For any one hole size, the venting rate will be constant until all the liquid is vaporized. This is consistent with the assumption of isothermal conditions in the tank and results in a worst case estimate of the gas venting rate, except perhaps in the case of a catastrophic release. The values presented in Figure 18 are independent of the tank car size, but assume that the temperature of the liquid is 40°C, yielding a saturated vapour pressure of 1600 kPa.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car (2.75 m ϕ x 13.4 m long) filled with ammonia at 40°C has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 1 minute and what is the instantaneous discharge rate from the tank?

Solution to Problem A

Step 1: Calculate amount remaining at t=1 min

- Use Figure 15
- With t=1 min and d=150 mm, the amount remaining is about 20 percent or 16 000 L

Step 2: Calculate the discharge rate

- Use Figure 16
- With d=150 mm, the instantaneous discharge rate (q) = 800 L/s

ii) Problem B

The standard tank car in Problem A has been punctured above the liquid level. The equivalent diameter of the orifice is estimated at 250 mm. How long will it take to empty the tank car and what is the release rate, assuming isothermal conditions?

FIGURE 17

AMMONIA (Anhydrous)

PERCENT REMAINING vs TIME

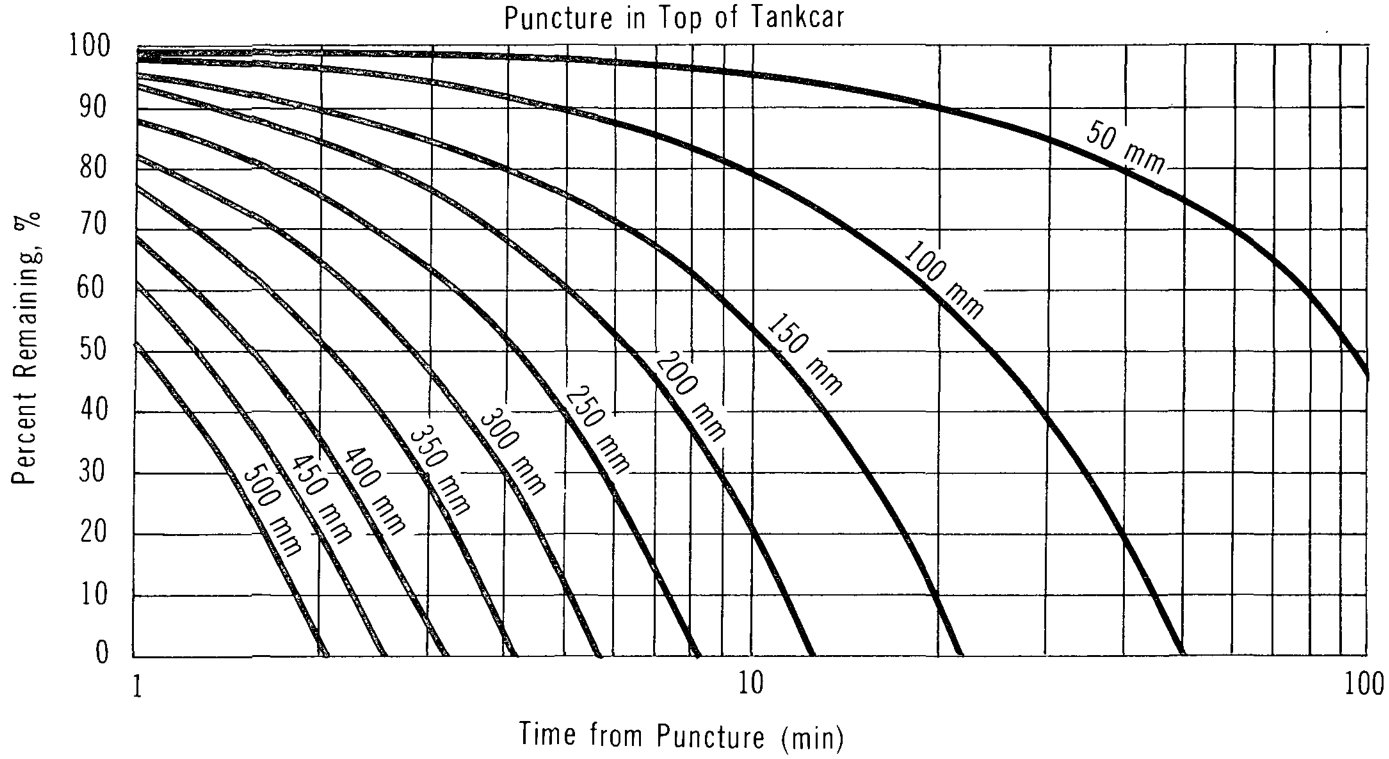
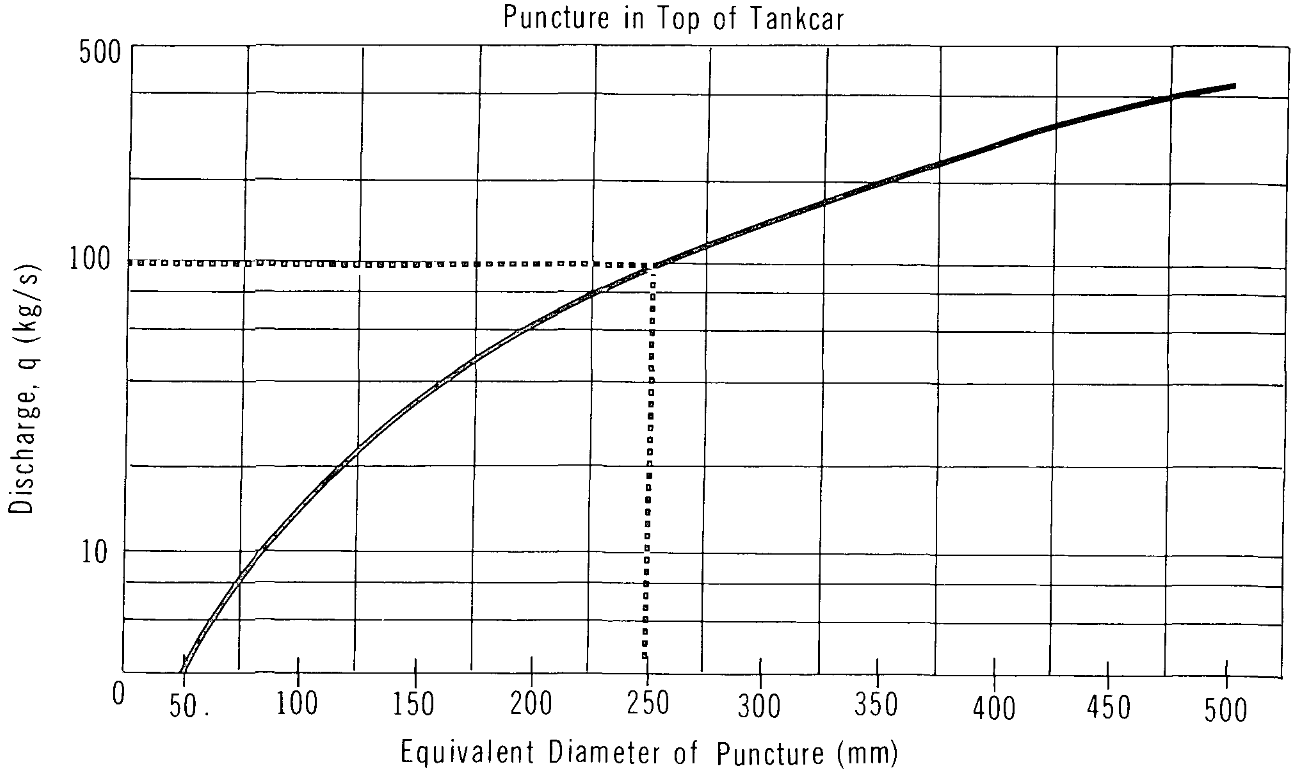


FIGURE 18

AMMONIA (Anhydrous)

DISCHARGE RATE vs PUNCTURE SIZE



Solution to Problem B

Step 1: Calculate the time to empty

- Use Figure 17
- With d=250 mm, the tank empties (0 percent remaining) in approximately 8 min

Step 2: Calculate the discharge rate

- Use Figure 18
- With d=250 mm and assuming isothermal conditions, the venting rate is constant at 100 kg/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since anhydrous ammonia under pressure is an extremely volatile liquid, vapour released from a liquid pool spilled on a ground or water surface vaporizes rapidly enough to consider the spill as producing instantaneous vapour in the form of a puff. Only this type of vapour release is treated here. It should be noted that the use of the "puff" release model for spills of anhydrous ammonia may overestimate the hazard as a result of the spill, since only about 20 to 50 percent of the instantaneously released liquid will flash off as a puff (Resplandy 1969).

It should also be noted that an ammonia vapour cloud arising from cold bulk liquid or droplets behaves as a heavier-than-air gas, even though the vapour density at ambient temperature would be less than that of air. This has been observed from actual and experimentally controlled spills. Conventional Gaussian formulas will tend to depict heavier-than-air plumes (puffs) to be narrower than observed. In the case of ammonia, this approach actually makes the results closer to the observed plumes because of the aerosol formed and its heavy gas behaviour. The environmental conditions and spill circumstances will influence the behaviour of the vapour cloud. For example, it has been shown experimentally that for the specific conditions of the experiment (liquid ammonia spilled onto water), the plume behaved as a gas that was less dense than air and rose while moving downwind (Raj 1978). In the case of an instantaneous release of 28.43 m^3 (7509 gal.) of liquid ammonia from a catastrophically damaged tanker truck, the resulting plume from the initial puff rose into the air, forming a condition that was considered the least harmful dispersion. The meteorological conditions at the time of the accident were: humid, temperature around 27-29°C, sunny, and a 3.13 m/s (7 mph) wind. At two other accident sites involving liquid ammonia spilled from railroad tank cars, the puff traveled more than 9 miles along the surface under a light steady wind in one case; in the other, the weather conditions produced a heavy ground concentration. In the former case, the initial release was afforded ideal conditions to effect a heavy initial ground concentration by the tree canopy at the accident site. The meteorological conditions at the former were: light rain, night, temperature about 20°C and a wind of 1.56 m/s (3.5 mph); conditions at the latter site were: strong temperature inversion and a temperature of 16.6°C. As noted earlier, recent studies lead one to the conclusion that heavy gas behaviour will be shown in circumstances where the atmospheric conditions are stable and temperature is low and/or where the spill is large; and that light gas behaviour will be shown where the atmospheric condition is less stable and temperature is high and/or the spill is smaller. The atmospheric conditions (stability and temperature) are probably the more important factors.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 19 depicts schematically the contaminant plume configuration from a "puff" surface release. The dispersion model represents the spill as an instantaneous point source, with a total vapour release quantity (Q_T) equal to the amount of contaminant spilled.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in order given):

Table 10:	weather conditions
Figure 21:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 11:	maximum puff hazard half-widths
Figure 24:	vapour puff travel distance as a function of time elapsed since the spill and wind speed

The flow chart given in Figure 20 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid

SCHEMATIC OF CONTAMINANT PUFF

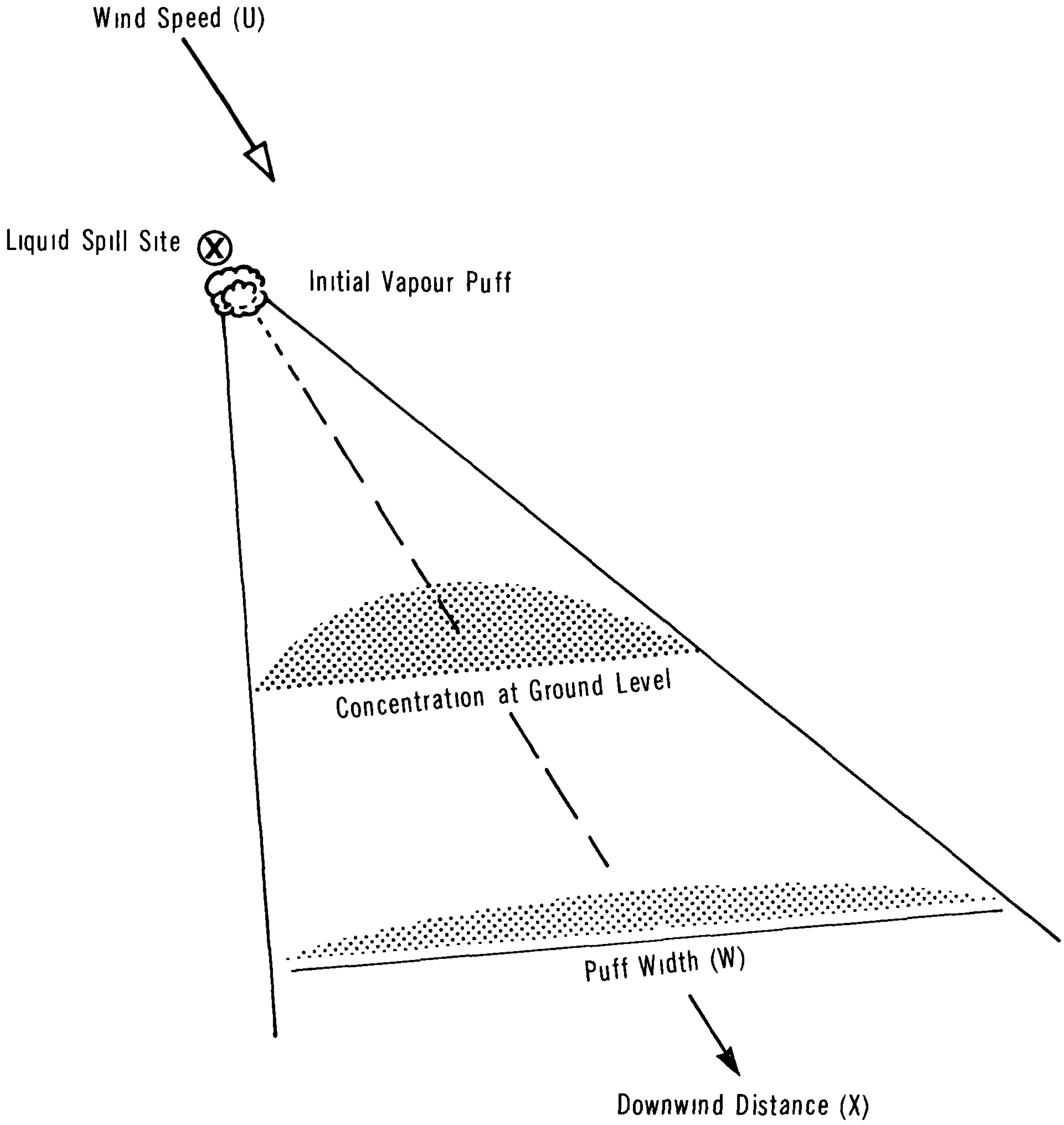
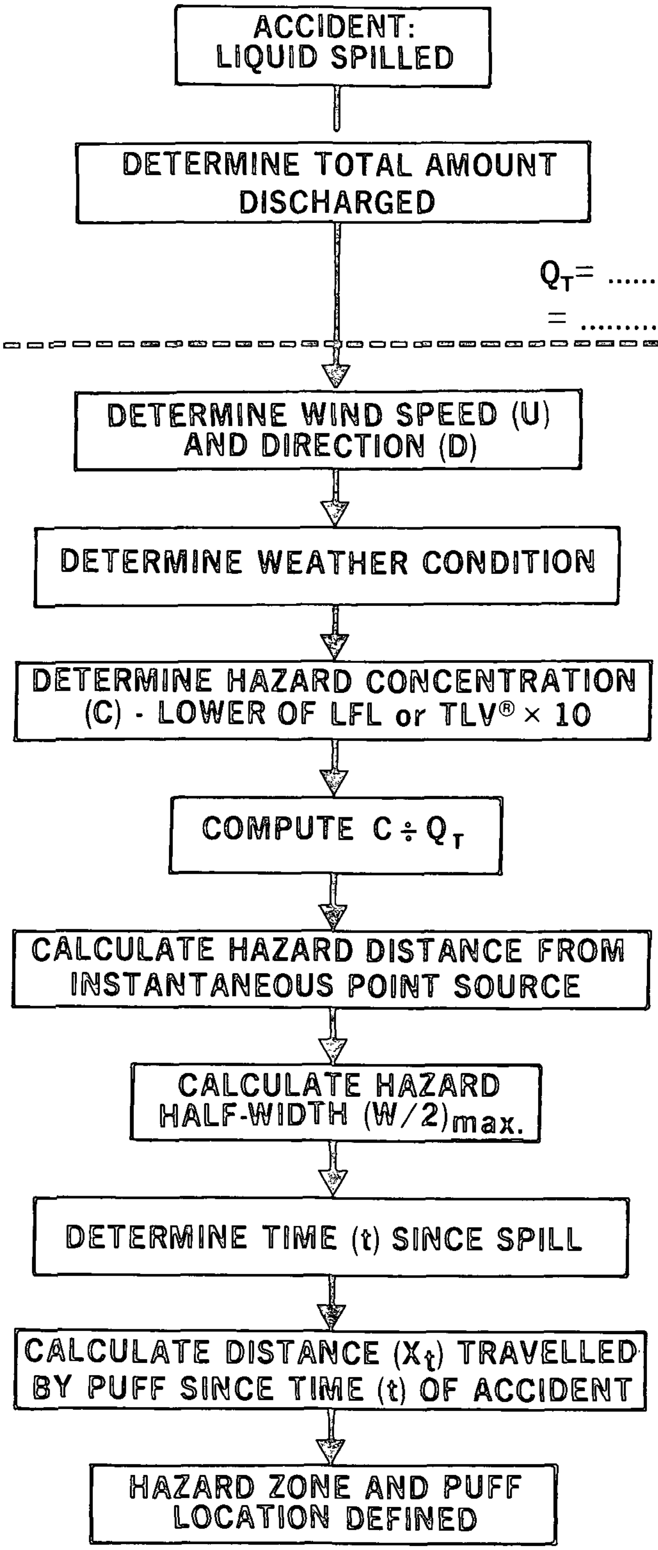


FIGURE 20

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE



Step 1: Use Figure 15 Section 5.2

Time since puncture .... minutes

Equivalent diameter of puncture ...... mm

Percent of chemical remaining .... %

Amount discharged:

q = 80 000 L − % × 80 000 L = ... L

Q_T = ... L × density (kg/L) ÷ 1000 = ... tonnes

= .... tonnes × 10^6 grams/tonne = ... grams

Step 2: Observed or estimated

U = ... km/h; D = ... degrees

Step 3: Use Table 10

Condition = ...

Step 4: C = 0.18 g/m³ for Ammonia
10 × TLV® (1981)

Step 5: Computation required

C/Q_T = ... m^{-3}

Step 6: Use Figure 21

X = ... km

Step 7: Use Table 11

$(W/2)_{max.}$ = ... m

Step 8:

t = ... s

Step 9: Use Figure 24
with U from Step 2

X_t = ... km

discharged" are contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 21: Vapour concentration versus downwind distance. Figure 21 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (C/Q_T) at the centreline of the contaminant puff. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 21, the weather condition must be determined from Table 10.

TABLE 10 WEATHER CONDITIONS

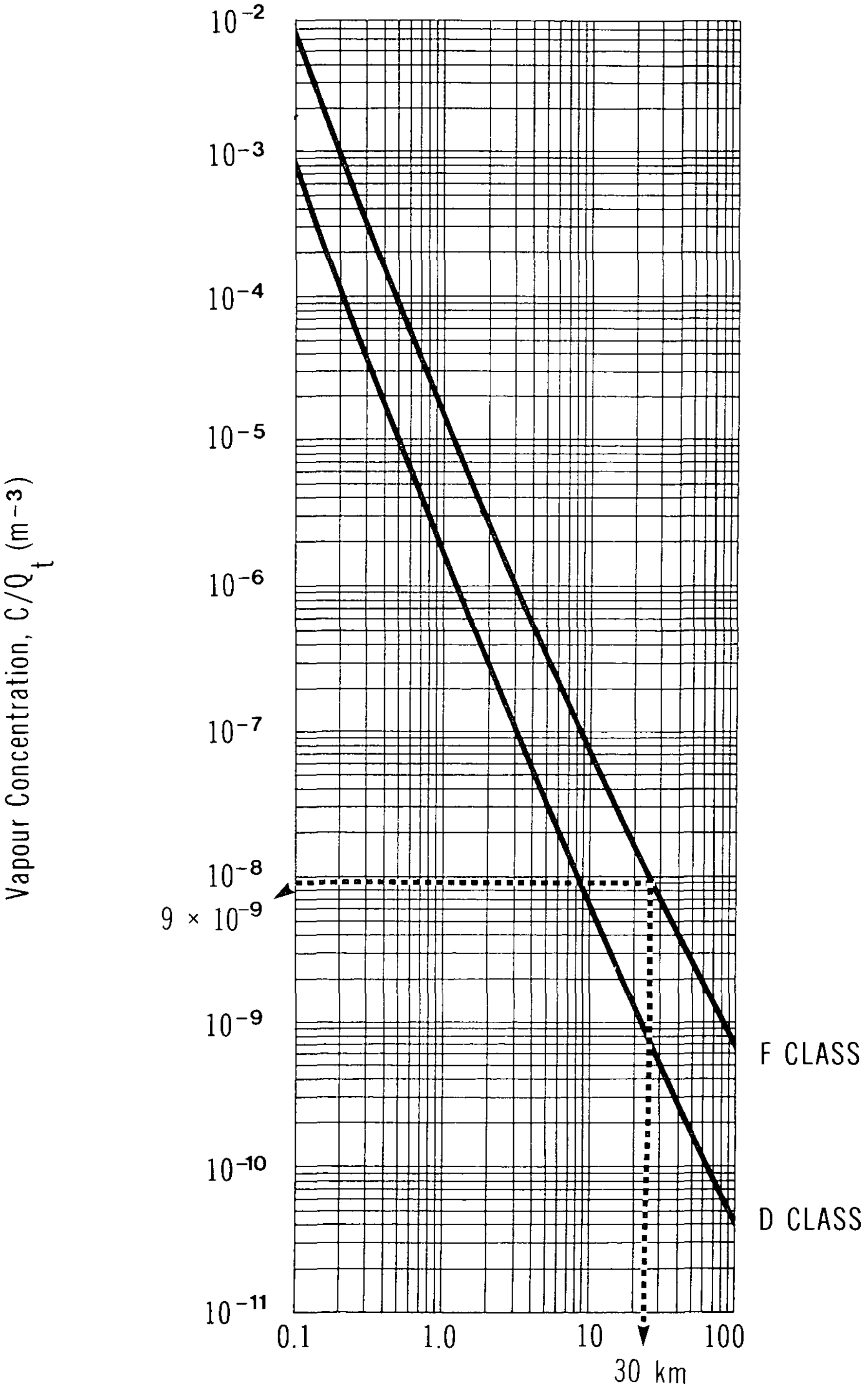
Weather Condition F	Weather Condition D
Wind speed < 11 km/h (≈3 m/s) and one of the following: - overcast day - night time - severe temperature inversion	Most other weather conditions

Use: The maximum hazard distance, X, downwind of the spill can be calculated from Figure 21 knowing:

- Q_T, the mass of vapour emitted (equivalent to liquid spilled)
- U, the wind speed (m/s)
- the weather condition
- The hazard concentration limit, C, which is the lower value of the Threshold Limit Value® (TLV, in g/m^3) or the Lower Flammability Limit (LFL, in g/m^3). Note: To convert the TLV®, (in ppm) and the LFL (in % by volume) to concentrations in g/m^3, use Figures 22 and 23

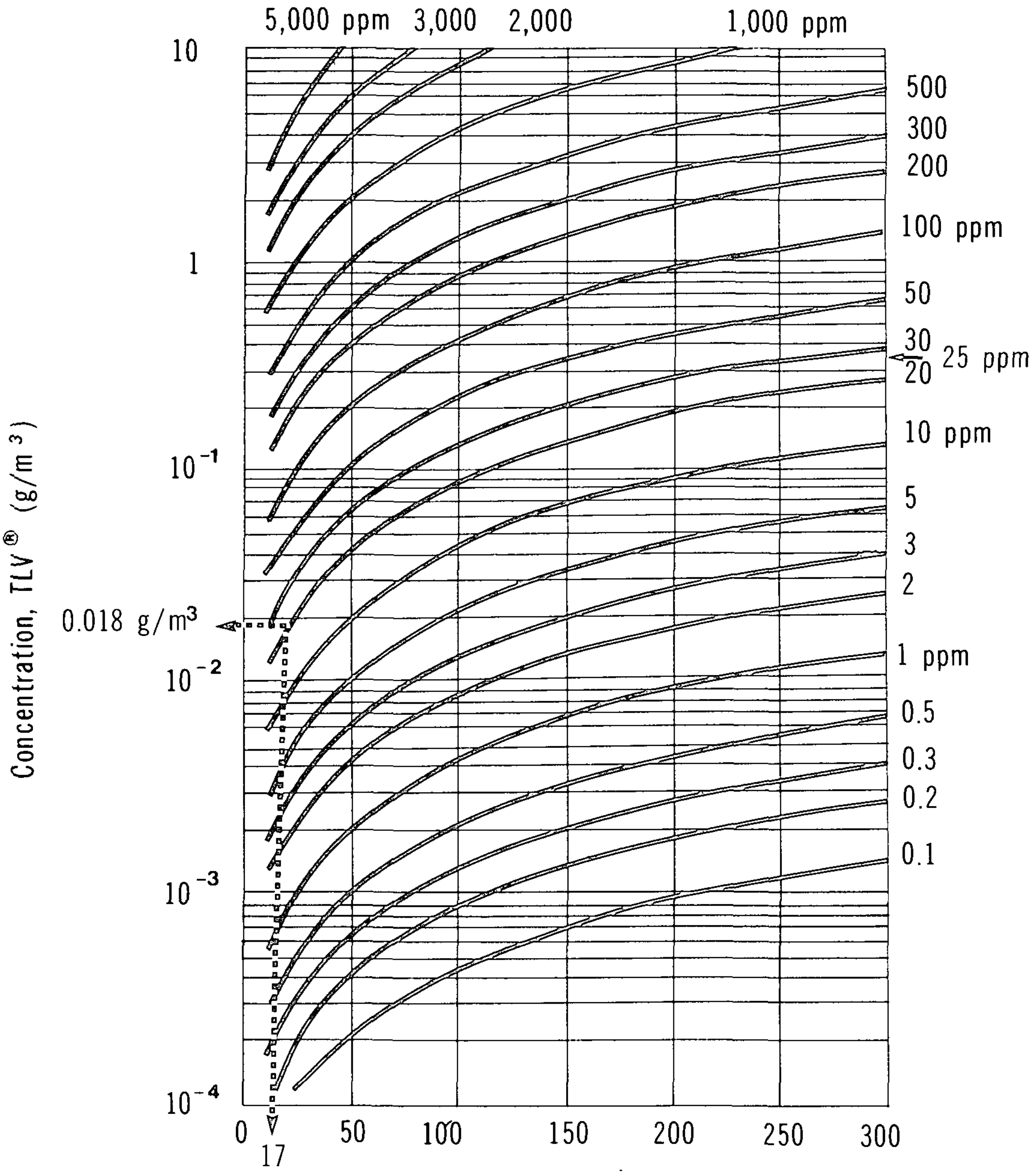
A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure and use of this value as the hazard limit would result in unrealistically

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



Maximum Downwind Hazard Distance, X (km)

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)

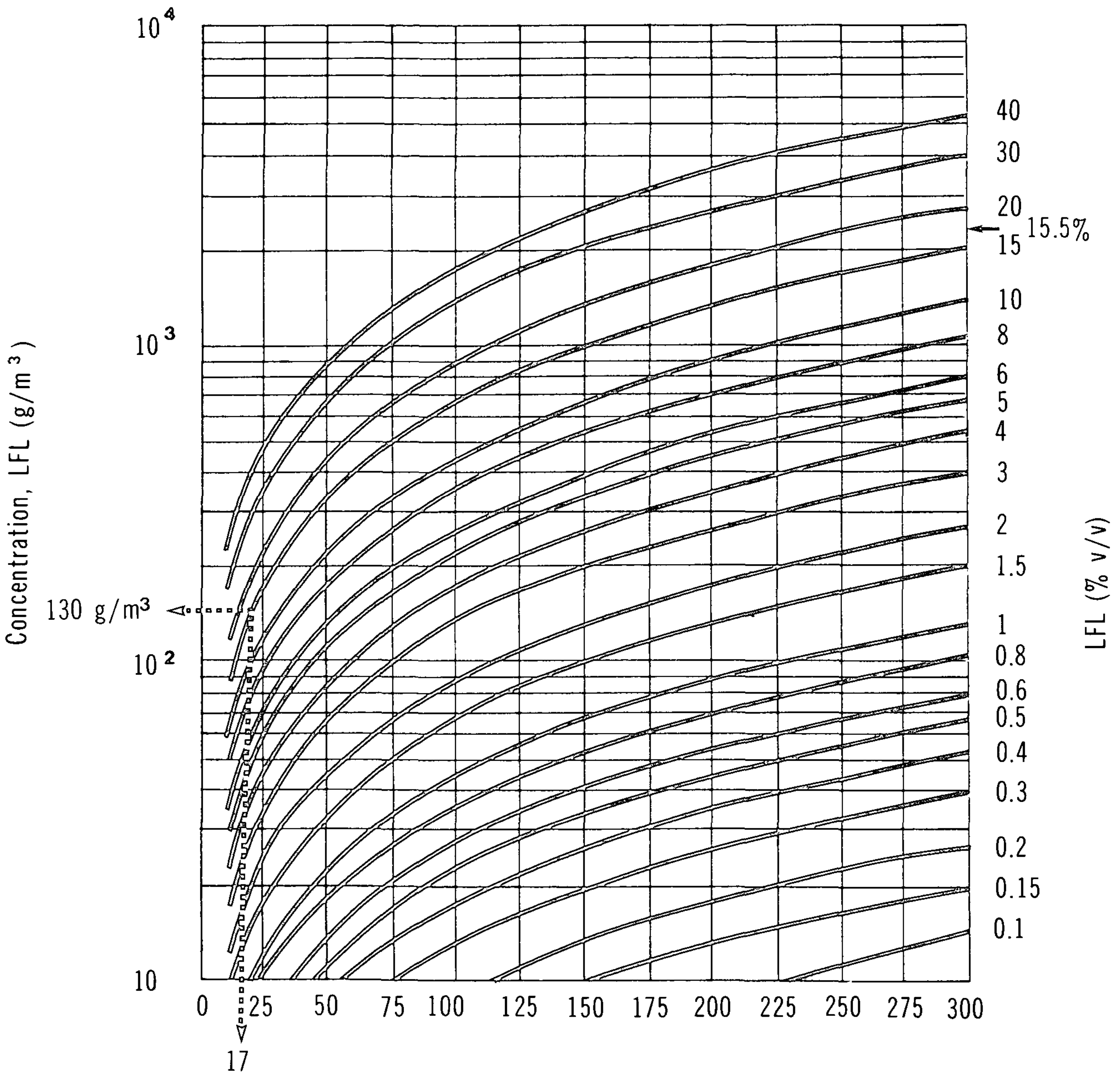


Molecular Weight

Example: Ammonia, MW = 17, TLV® = 25 ppm,
then TLV® in g/m³ = 0.018

Note: data applicable at 25° and 760 mm Hg pressure

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example: Ammonia, MW = 17, LFL = 15.5%,
then LFL in g/m³ = 130

Note: data applicable at 25°C and 760 mm Hg pressure large hazard zones. It should be noted that irritation effects have been noted at 10 times the TLV® (250 ppm or 180 mg/m^3), as noted in Chapter 7.

5.3.2.2 Table 11: Maximum puff hazard half-widths. This table presents data on the maximum puff hazard half-width, $(W/2)_{max}$, for a range of Q_T values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the ammonia Threshold Limit Value (TLV®) of 0.018 g/m^3, or 0.18 g/m^3. The maximum puff hazard half-width represents the maximum half-width of the ammonia vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 11 is therefore only applicable for an ammonia hazard concentration limit of 10 x TLV®, or 0.18 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of instantaneous vapour emission rates (Q_t) used was 0.01 to 5800 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spills, the mass spilled would be 54 500 kg or approximately 55 tonnes. Therefore, under class D of Table 11, data are provided for up to 105 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.01 to 275 tonnes, respectively. Therefore, under class F of Table 11, data are provided for up to 5 times a standard rail car load.

Use: Knowing the weather condition and Q_T, pick the closest value in the table and the corresponding $(W/2)_{max}$, the maximum puff hazard half-width, in metres. (For intermediate numbers, interpolate Q_T and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 11.

5.3.2.3 Figure 24: Puff travel time versus travel distance. Figure 24 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the puff has travelled.

5.3.3 Sample Calculation. The sample calculation given is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid ammonia. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here

TABLE 11 MAXIMUM PUFF HAZARD HALF-WIDTHS (FOR AMMONIA)

Weather Condition D			Weather Condition F		
Q_T (tonnes)	$(W/2)_{max}$ (m)		Q_T (tonnes)	(W/2) (m)	
5800	4030	(99.5 km)*	275	1870	(100 km)*
5500	3950		250	1810	
5000	3810		200	1640	
4000	3500		150	1450	
3000	3130		100	1220	
2000	2680		75	1075	
1500	2400		50	905	
1000	2060		30	730	
800	1890	Q_T = 20 tonnes→	20	610	$(W/2)_{max}$ = 610 m
600	1690		10	455	
400	1450		7.5	410	
300	1300		5	345	
200	1110		2	240	
150	1000		1	185	
100	855		0.75	165	
50	660		0.5	140	
20	475		0.2	100	
10	365		0.1	75	
5	280		0.075	70	
2	200		0.05	60	
1	155		0.01	33	
0.5	120				
0.2	85				
0.1	70				
0.05	55				
0.01	30				

* Data are provided up to a maximum downwind hazard distance of 100 km

Example: Under weather condition F and Q_T = 20 tonnes, then puff hazard half-width $(W/2)_{max}$ = 610 m

Note: Above table is valid only for an ammonia concentration of 10 x TLV®, or 0.18 g/m^3.

apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill quantity) in a particular spill situation if possible.

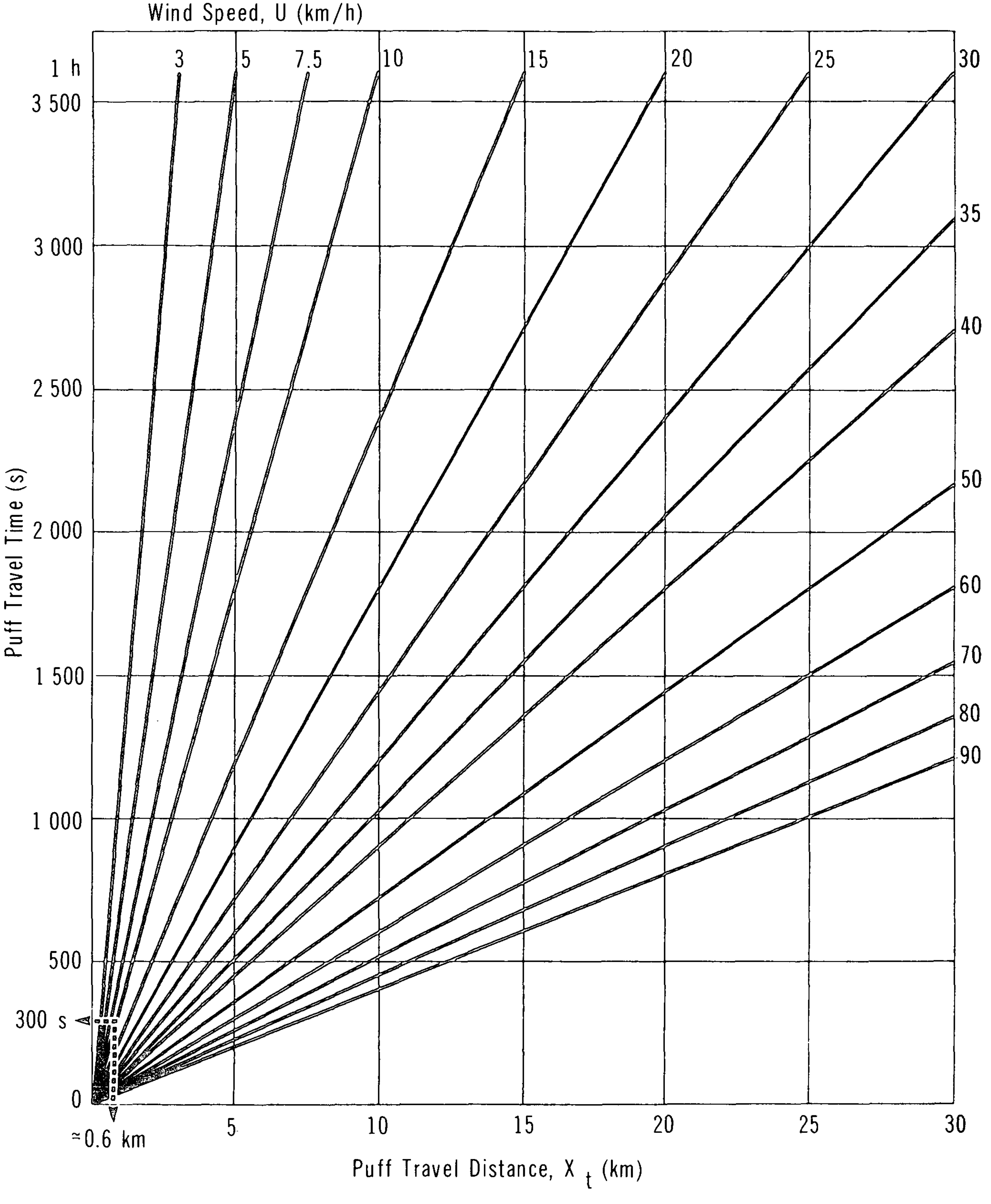
Problem:

During the night, at about 2:00 a.m., 20 tonnes of anhydrous ammonia were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

FIGURE 24

AMMONIA

PUFF TRAVEL TIME
VS TRAVEL DISTANCE



Solution

Step 1: Quantity spilled is given, Q_t = 20 tonnes

- Q_T = 20 tonnes or 20 x 10^6 g
- Q_T = 2 x 10^7g

Step 2: Determine wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given:

  U = 7.5 km/h, then U = 7.5 / 3.6 = 2.1 m/s

  D = NW or 315° (D = Direction from which wind is blowing)

Step 3: Determine weather condition

- From Table 10, weather condition = F since U is less than 11 km/h and it is night

Step 4: Determine hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL, so for ammonia

  C = 0.18 g/m^3 (TLV® = 0.018 g/m^3; LFL = 130 g/m^3)

Step 5: Compute C/Q_T

- $C/Q_T = \frac{0.18}{2 \times 10^7} = 9 \times 10^{-9}\ m^{-3}$

Step 6: Calculate downwind hazard distance (X) from the instantaneous point source

- From Figure 20 with C/Q_T = 9 x 10^{-9} m^{-3} and weather condition F, X ≃ 30 km

Step 7: Calculate puff hazard half-width, $(W/2)_{max}$

- Use Table 11
- With Q_T = 20 tonnes
- Then for weather condition F, $(W/2)_{max}$ = 610 m

Step 8: Determine time since spill

- t = 5 min x 60 = 300 s

Step 9: Calculate distance travelled (X_t) by vapour puff since time of accident

- Using Figure 24 with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from X_t = Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 10: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (640 m) by the maximum hazard distance downwind of the instantaneous point source (30 km) along the direction of the wind, as shown in Figure 25
- If the wind is reported to be fluctuating by 20° about 315° (or from 315° ± 10°), the zone is defined as shown in Figure 26
- Note that the puff has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 235 minutes before the puff reaches the maximum downwind hazard distance of 30 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on water, liquefied ammonia will boil violently and partially vaporize; at the same time, it will spread on the surface and dissolve. Ammonia is readily dissolved in water, forming an aqueous solution. It has already been pointed out that around 70 percent (or less) of a mass spilled in water would dissolve.

For the purpose of nomogram preparation, two worst case situations have been assumed. First, the extent of spread on the surface of the water has been estimated, assuming that none of the ammonia is dissolved in the water. However, the loss due to vaporization has been taken into account. Secondly, the water pollution hazard has been evaluated by assuming all of the ammonia is dissolved in water and no vaporization occurs. These two cases represent the worst case situations for the extent of spread of ammonia on the surface of water and for the water pollution hazard associated with ammonia dissolved in water.

5.4.2 Spreading on Water. The rate of spreading on water is based on the balance of forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces). Since cryogenic liquids such as ammonia are evaporated quickly, only the initial gravity-inertia regime of spread is considered relevant (Raj 1974). The maximum size of the spill pool depends to a large extent on the rate of vaporization.

The equations representing the spreading of the spill on water are presented in the Introduction Manual. For the purposes of the nomogram presented, the water temperature has been taken at 20°C, representing a reasonable maximum for surface water bodies. This condition maximizes the spill size. No dissolution is assumed for this case.

FIGURE 25

AMMONIA

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

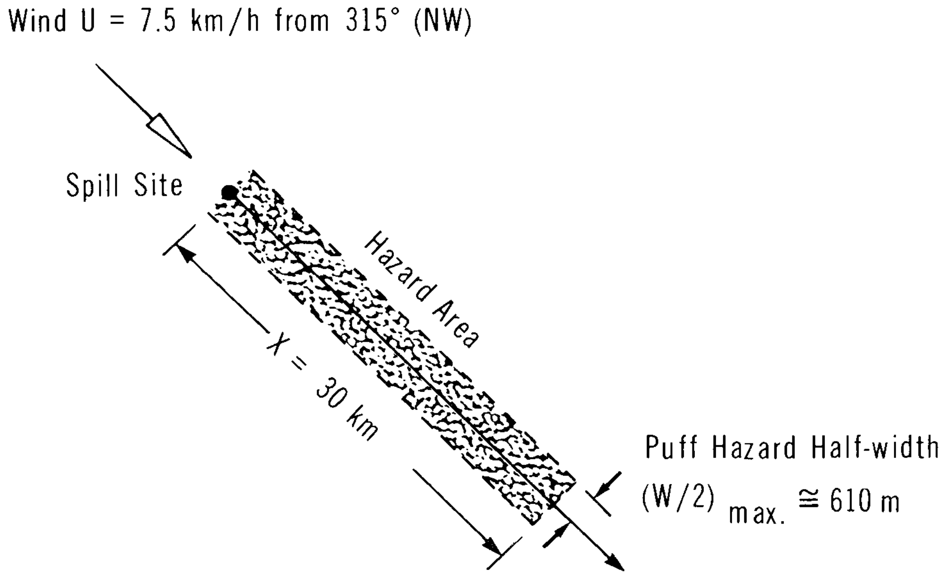
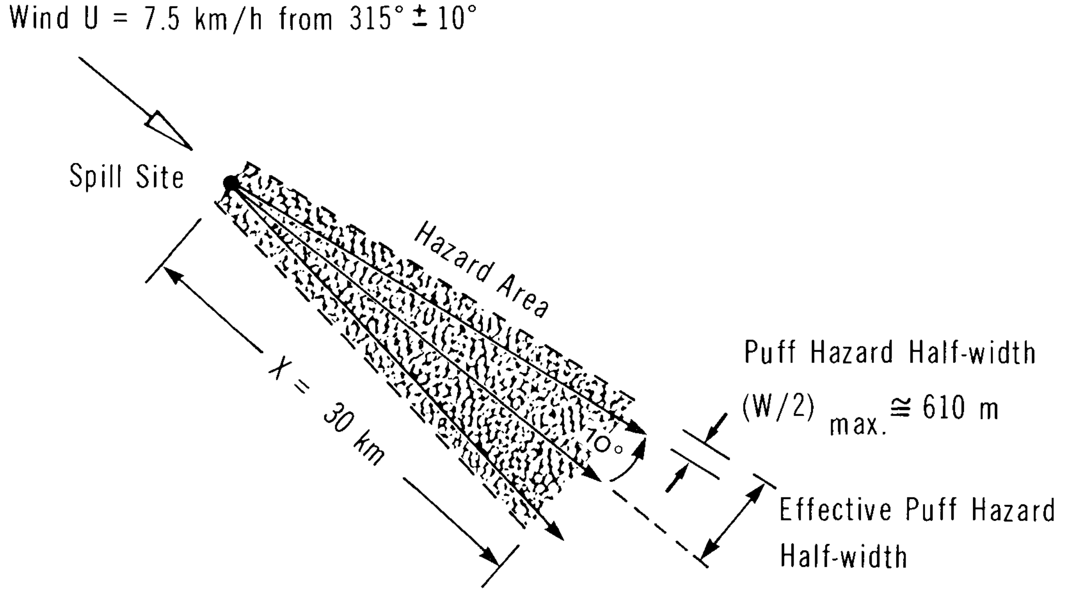


FIGURE 26

AMMONIA

HAZARD AREA FOR UNSTEADY WINDS , EXAMPLE PROBLEM



$= X \times 1000 \times \tan 10° + (W/2)_{max.}$

$= 30 \times 1\,000 \times \tan 10° + 610$ m

$= 5\,900$ m or 5.9 km

5.4.3 Dissolution in Water. For this condition, all of the spilled ammonia is assumed to dissolve rapidly without any vaporization. Mixing takes place and the spill is diluted. This mixing can generally be described by classical diffusion equations, with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence, while in calm water mixing takes place by molecular diffusion.

To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The model employed is strictly applicable to neutrally buoyant liquids and solids that dissolve in water. As ammonia is less dense than water, the maximum concentration would be expected near the surface.

The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 ($W/d < 100$) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.4 Nomograms. The following nomograms are presented to calculate spreading on still water (without dissolution) and to estimate pollutant concentrations in non-tidal rivers and in lakes (without vaporization).

Spreading on Still Water

Figure 27:	maximum spill radius versus spill size with estimated times for complete evaporation

Dissolution in Water - Non-tidal Rivers

Figure 29:	time versus distance for a range of average stream velocities
Figure 30:	hydraulic radius versus channel width for a range of stream depths
Figure 31:	diffusion coefficient versus hydraulic radius for a range of average stream velocities
Figure 32:	alpha* versus diffusion coefficient for various time intervals
Figure 33:	alpha versus delta* for a range of spill sizes

---

* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

Figure 34:	maximum concentration versus delta for a range of river cross-sectional areas

Dissolution in Lakes or Still Water Bodies

Figure 35:	volume versus radius for the hazard zone for a range of lake depths
Figure 36:	average concentrations versus volume for the hazard zone for a range of spill sizes

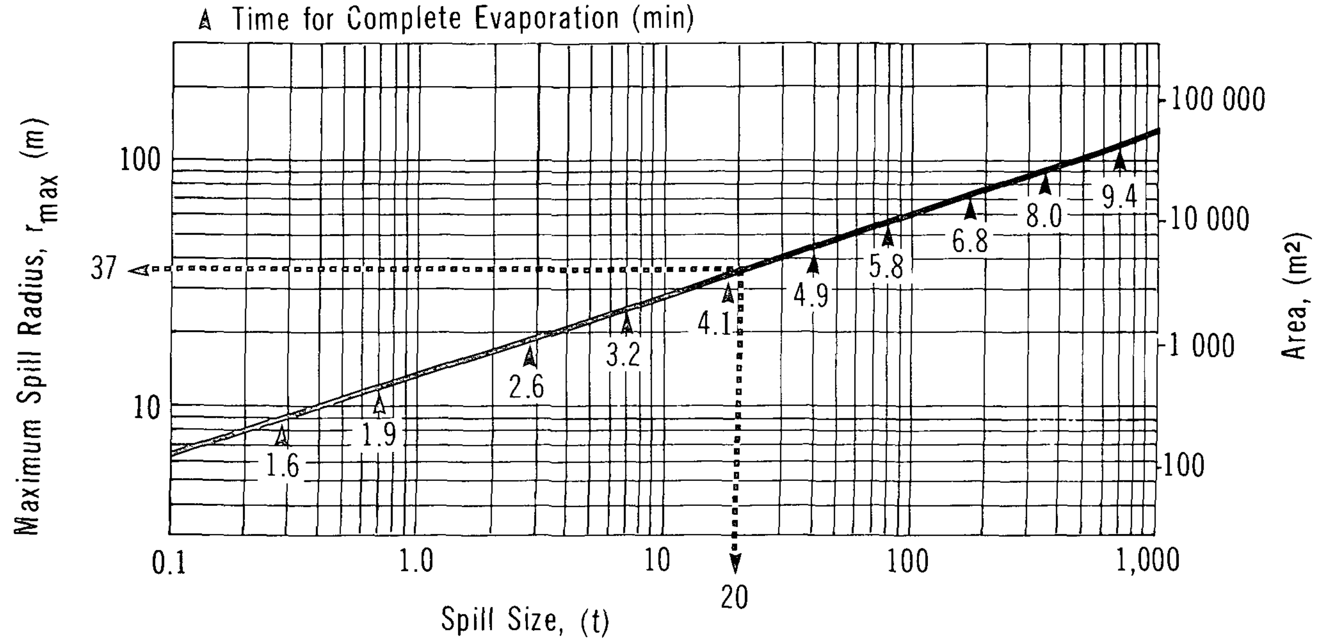
5.4.4.1 Nomogram for spreading on still water.

Figure 27: Maximum spill radius versus spill size. Assuming no dissolution in water, Figure 27 provides a simple means of estimating the maximum spill radius for ammonia, if the spill size is known. The nomogram is based on data presented in the Hazard Assessment Handbook (CHRIS 1974) and is based on a computer model for simultaneous spreading and evaporation of a cryogenic liquid spilled on water (Raj 1974). The bracketed figures on the nomogram provide an estimate of time for complete evaporation of the spill. Because of the short times involved, the complete time history of the spread of the spill has not been considered. Similarly, the translation distance of the spill by wind or surface current is not applicable.

FIGURE 27

AMMONIA (Anhydrous)

MAXIMUM SPILL RADIUS VS SPILL SIZE



5.4.4.2 Nomograms for dissolution in water - non-tidal rivers. The flow chart in Figure 28 outlines the steps required to estimate the downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 29 through 34) are described in the following subsections.

Figure 29: Time versus distance. Figure 29 presents a simple relationship between average stream velocity, time and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest, at some distance (X) downstream of the spill, can be readily obtained from Figure 29.

Figure 30: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentrations is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 30 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 31: Diffusion coefficient versus hydraulic radius. Figure 31 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 30 and the average stream velocity (U).

Figure 32: Alpha versus diffusion coefficient. Figure 32 is used to estimate a conversion factor alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 33: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 33 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

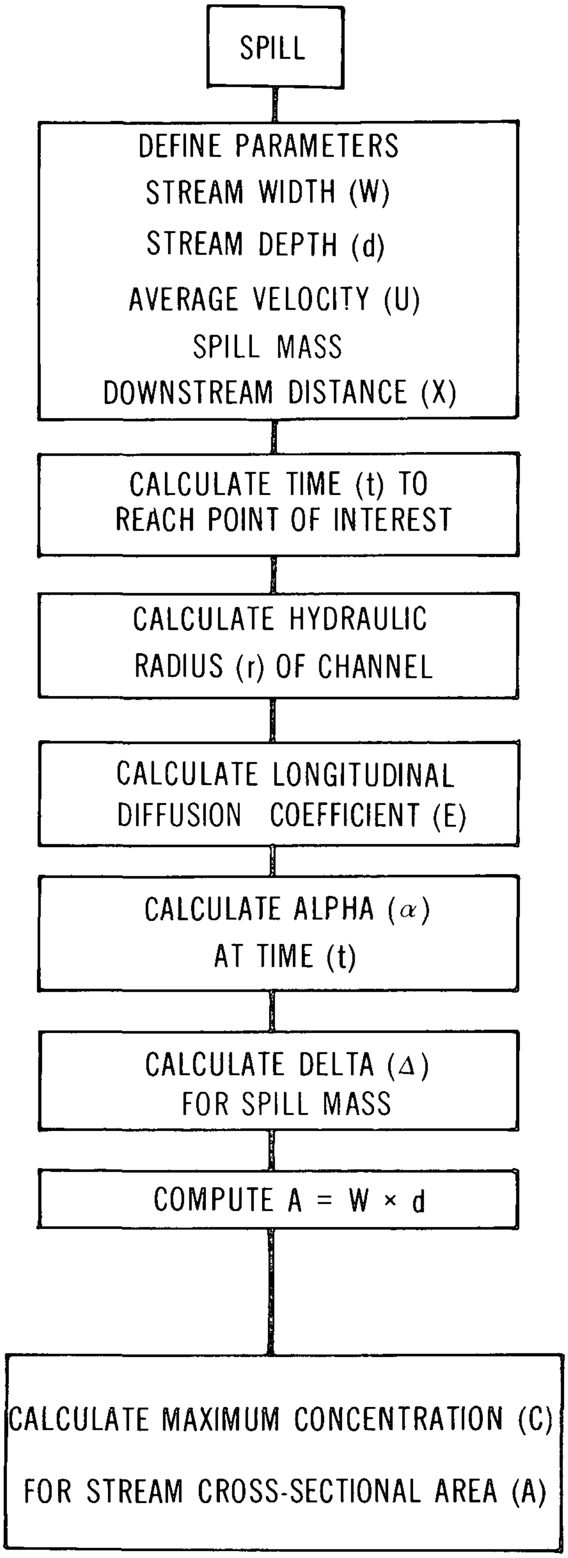
Figure 34: Maximum concentration versus delta. Figure 34 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 34 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.4.3 Nomograms for lakes or still water bodies.

Figure 35: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water

FIGURE 28

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS



Step 1: Observed or Estimated

W = __________ m

d = __________ m

U = __________ m/s

MASS = __________ tonnes

X = __________ m

Step 2: Use Figure 29

t = __________ minutes

Step 3: Use Figure 30

r = __________ m

Step 4: Use Figure 31

E = __________ m^2/s

Step 5: Use Figure 32

α = __________

Step 6: Use Figure 33

Δ = __________

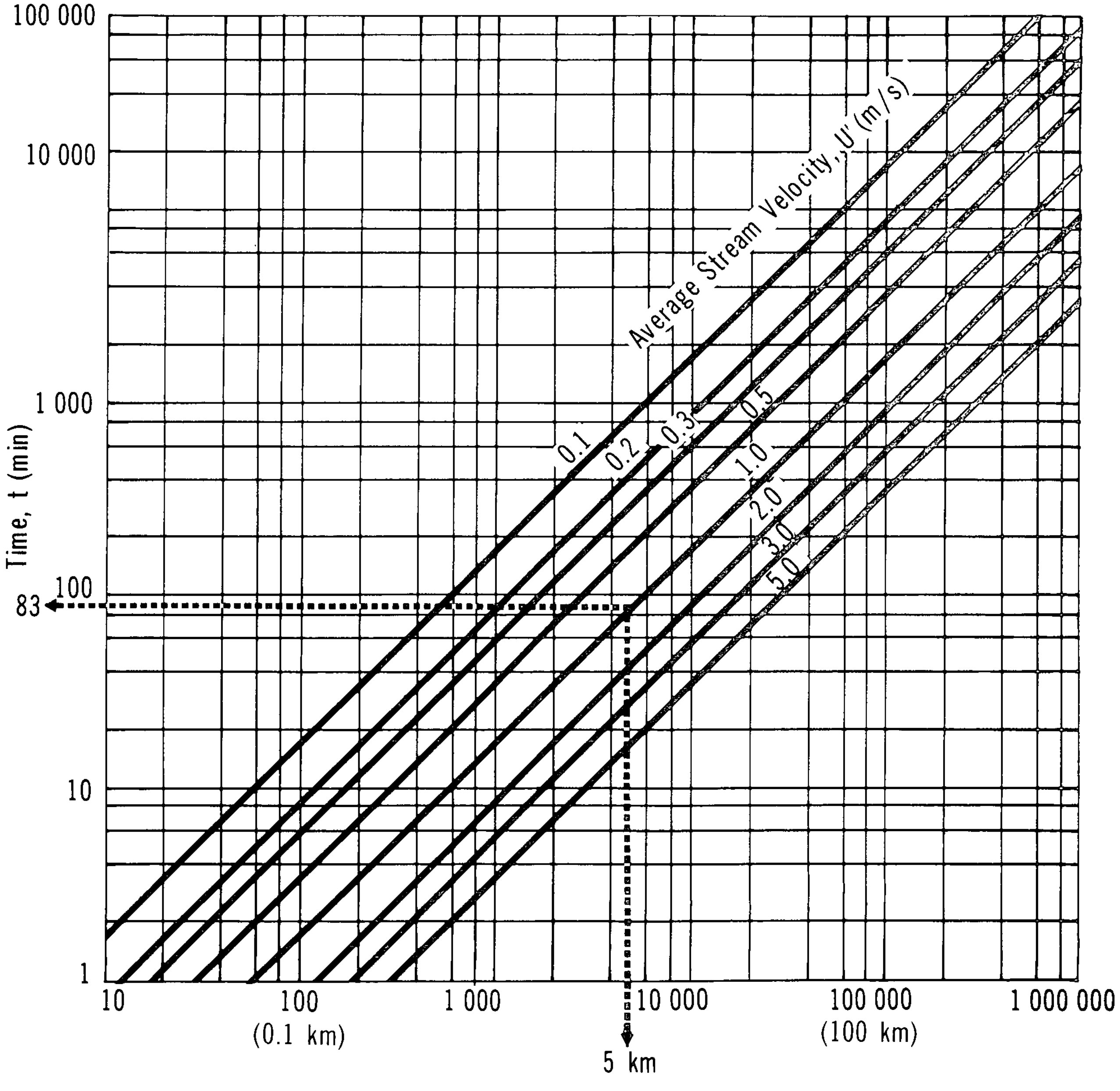
Step 7: Compute stream cross-sectional Area (A)

A = W × d _____ m^2

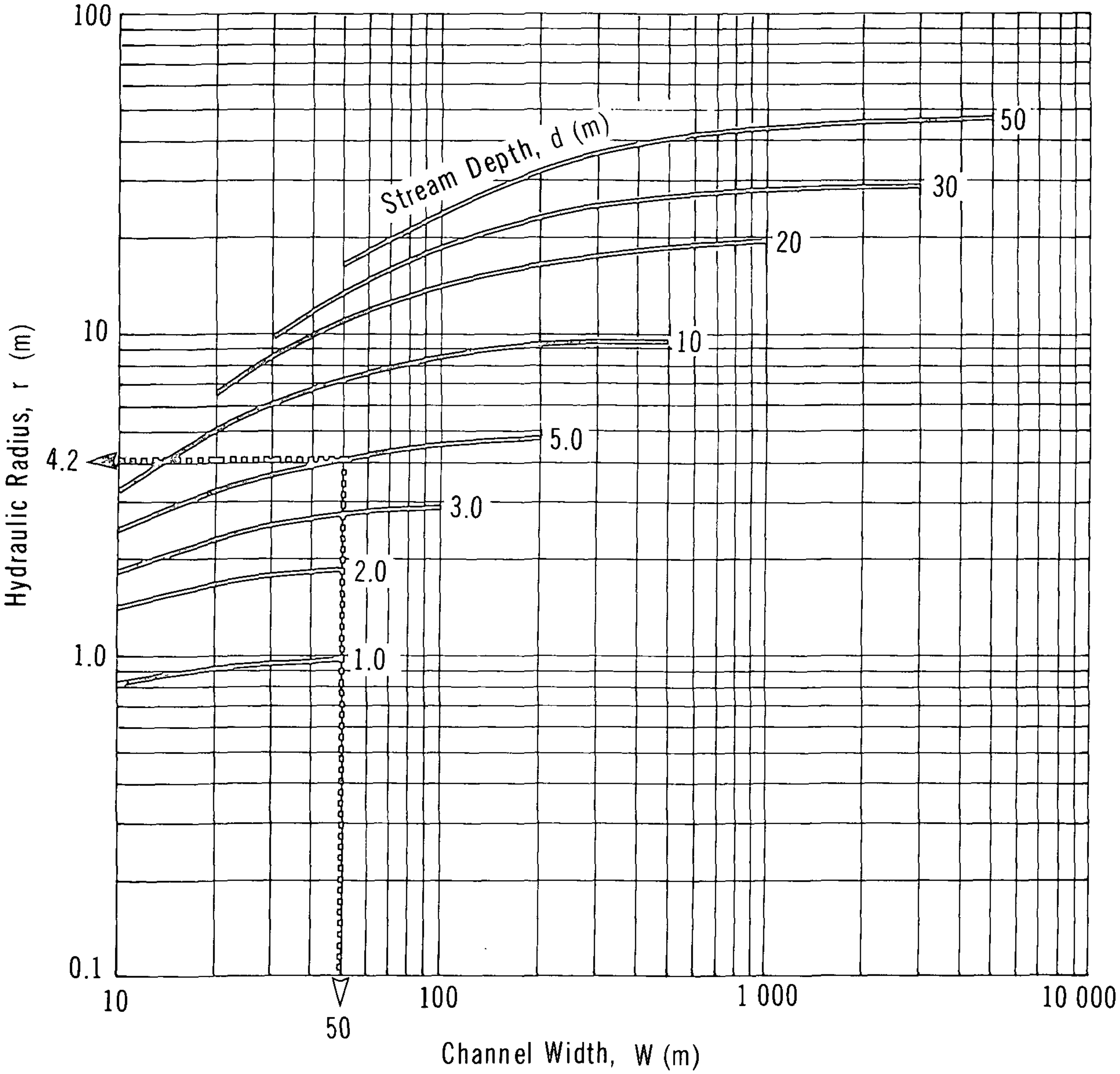
Step 8: Use Figure 34

C = __________ ppm

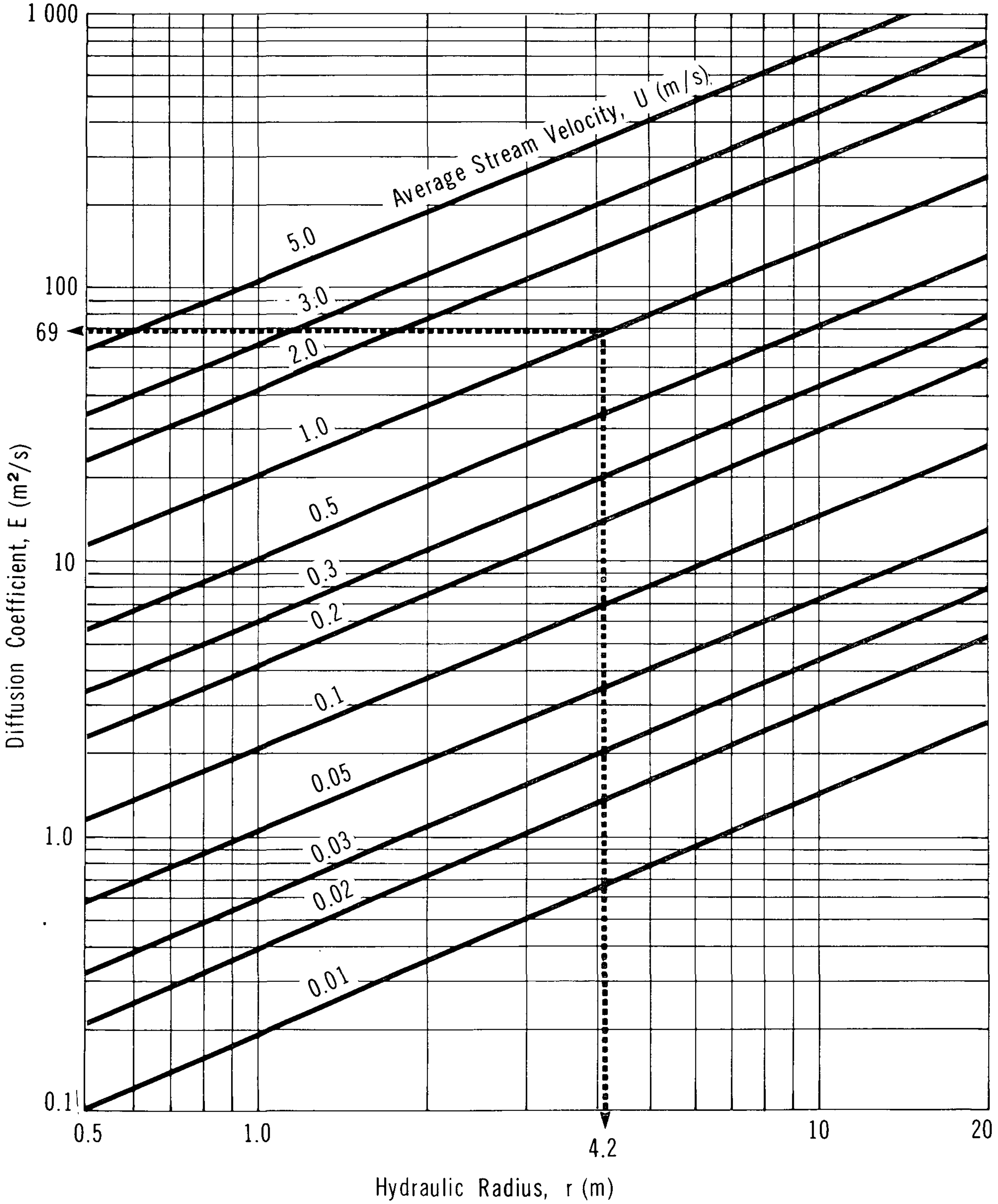
TIME vs DISTANCE



HYDRAULIC RADIUS VS CHANNEL WIDTH

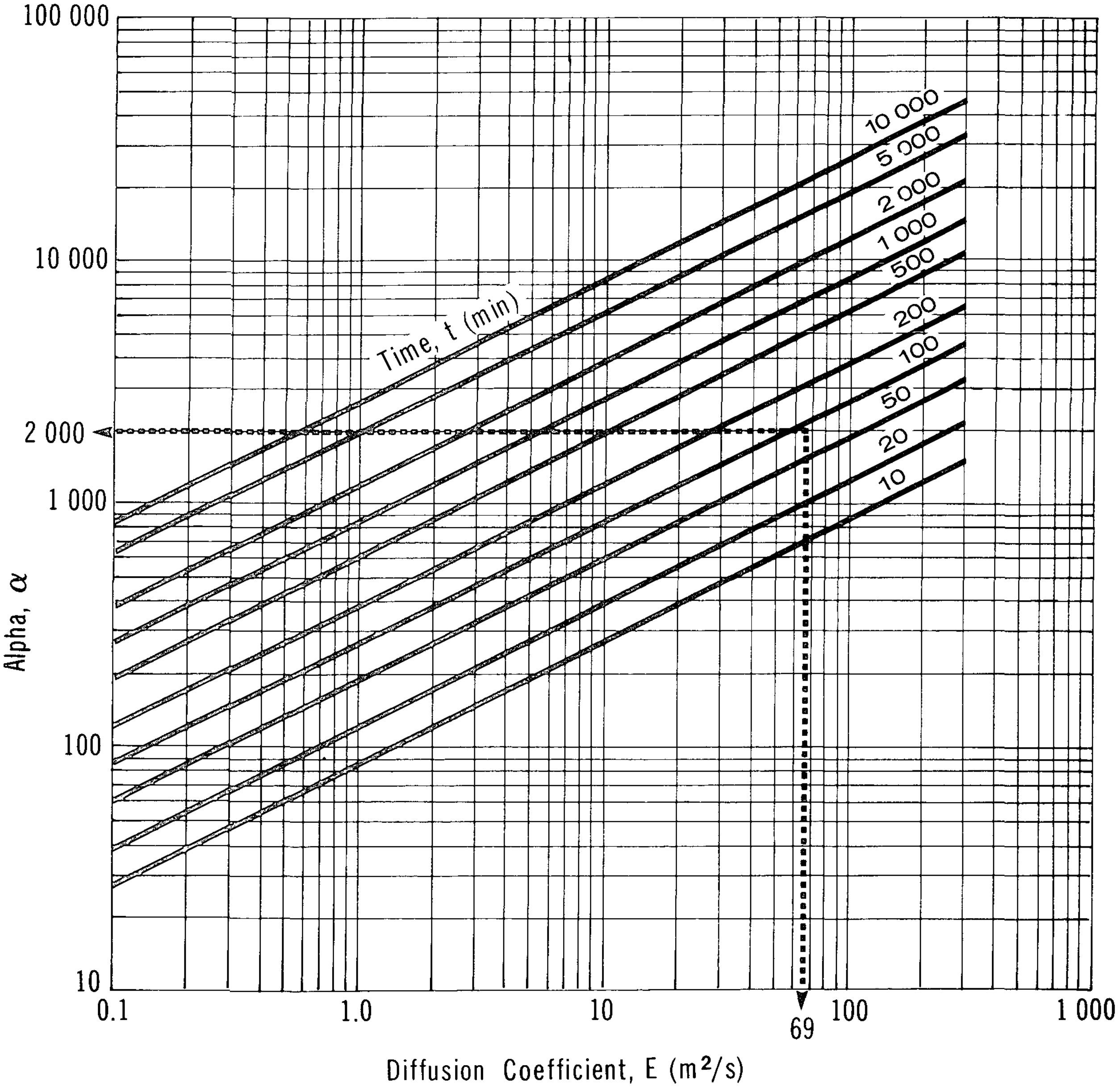


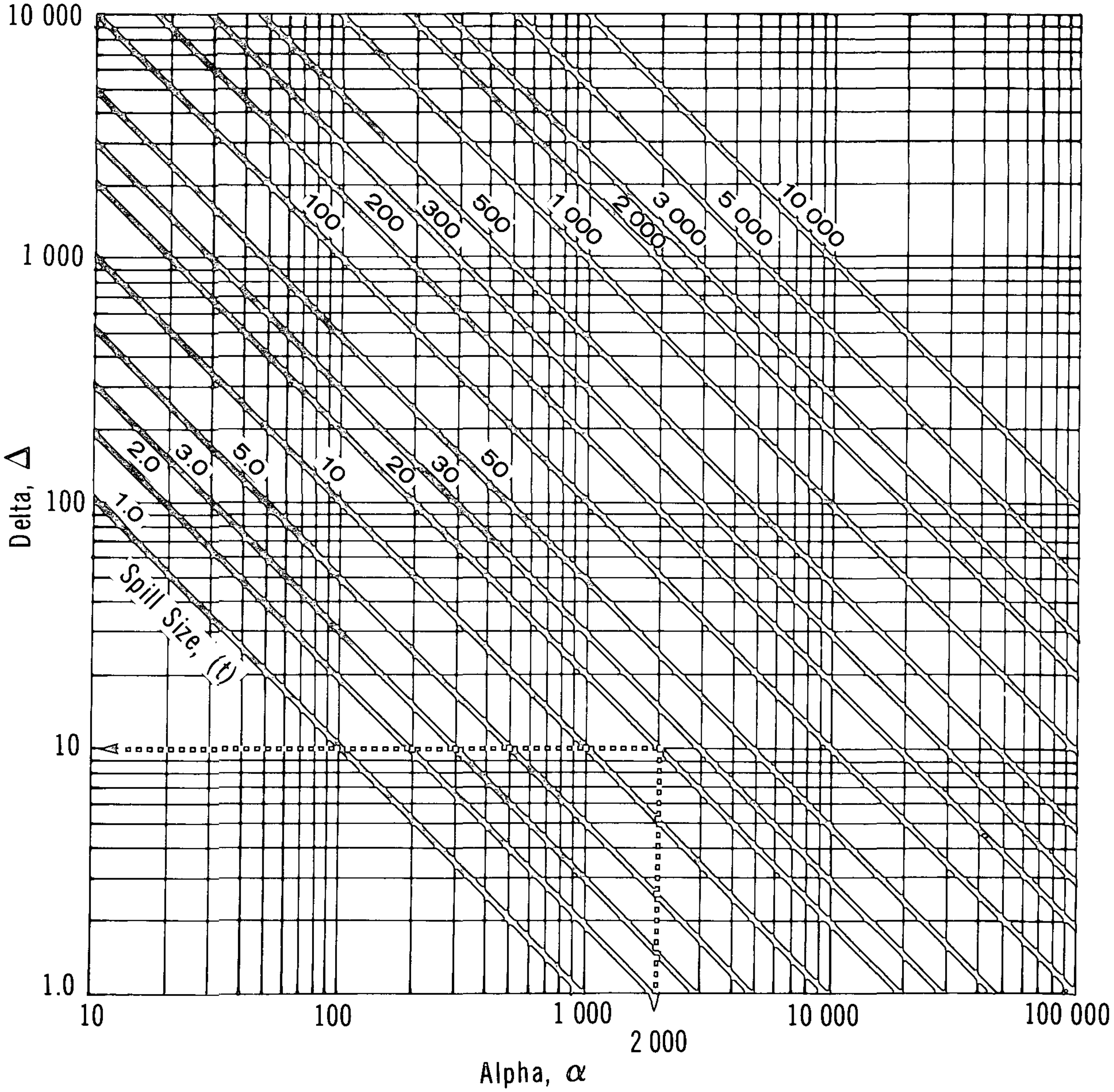
DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS



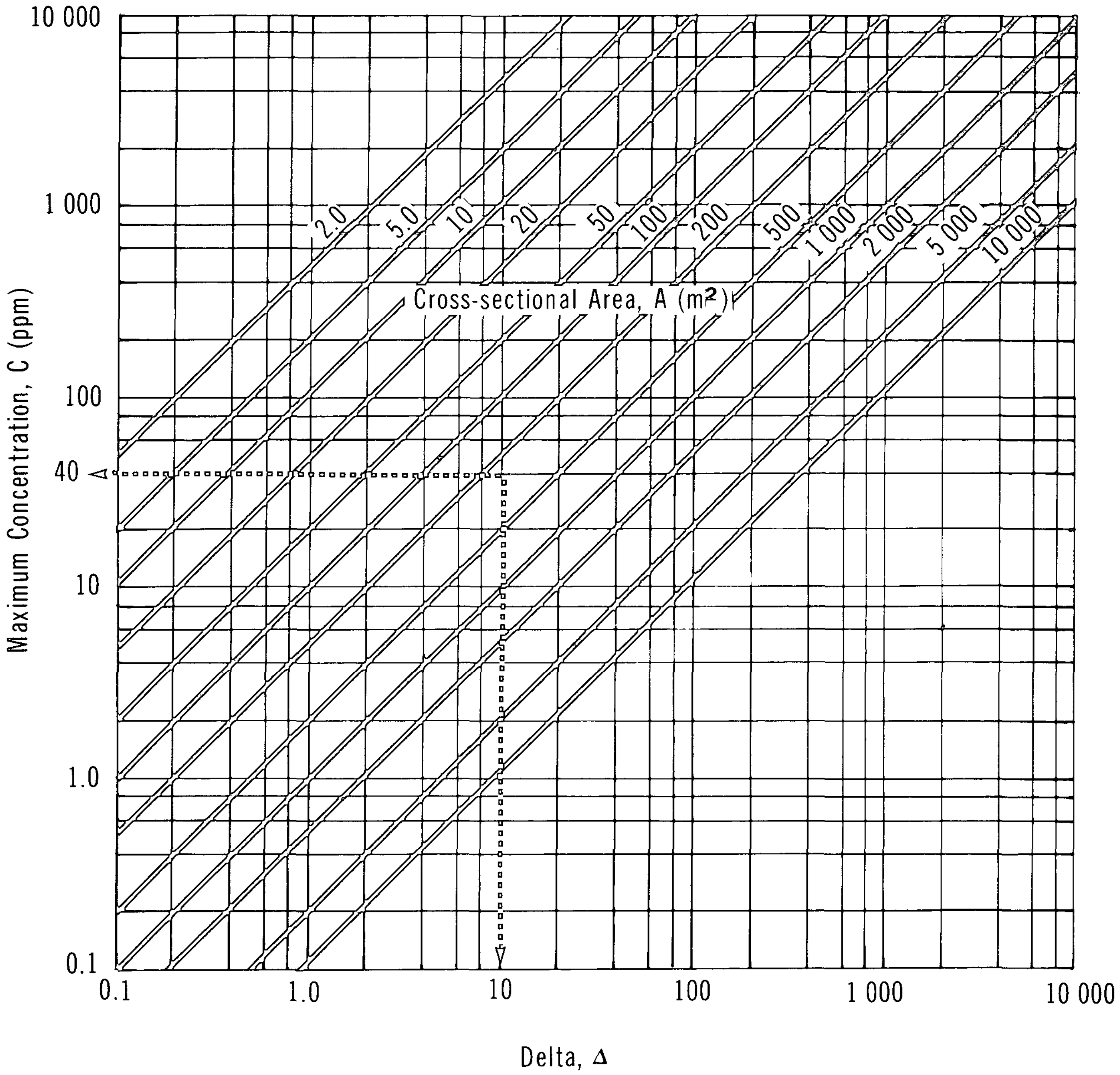
AMMONIA

ALPHA vs DIFFUSION COEFFICIENT

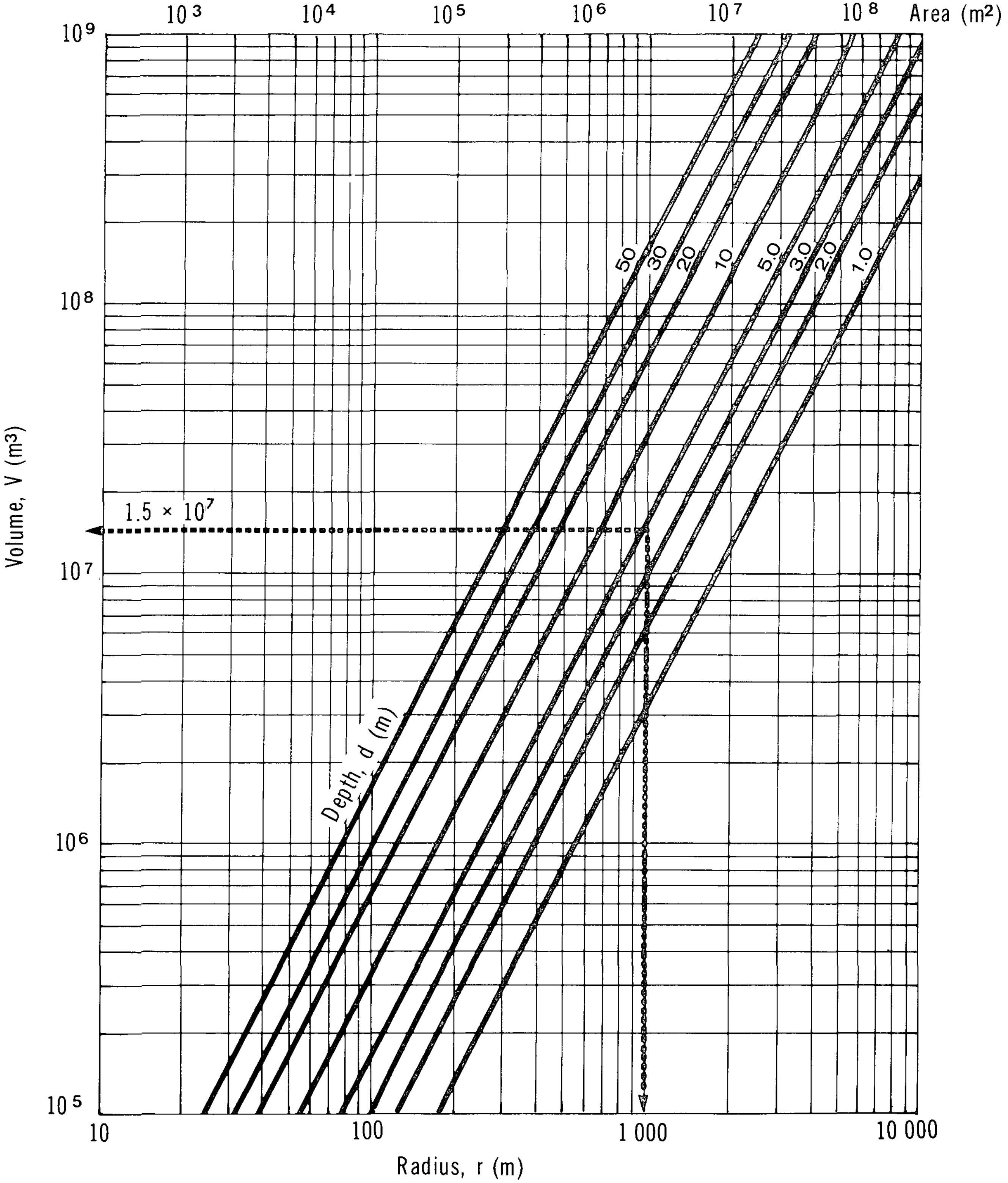



10 000
1 000
100
10
1.0
Delta, Δ
10
100
1 000
2 000
10 000
100 000
Alpha, α
Spill Size, (t)
1.0
2.0
3.0
5.0
10
20
30
50
100
200
300
500
1 000
2 000
3 000
5 000
10 000

MAXIMUM CONCENTRATION vs DELTA



VOLUME vs RADIUS



in the cylinder can be obtained from Figure 35. The radius (r) represents the distance from the spill to the point of interest.

Figure 36: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 36 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.5 Sample Calculations.

5.4.5.1 Spread on still water. A 20 tonne spill of ammonia has occurred on a large lake. What is the maximum size of the spill (assuming no dissolution) and approximate time for complete evaporation?

Solution

- Use Figure 27
- With spill mass = 20 tonne, r_{max} = 37 m
- Time for complete evaporation is a little over 4 min

5.4.5.2 Pollutant concentration in non-tidal river. A 20 tonne spill of ammonia has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

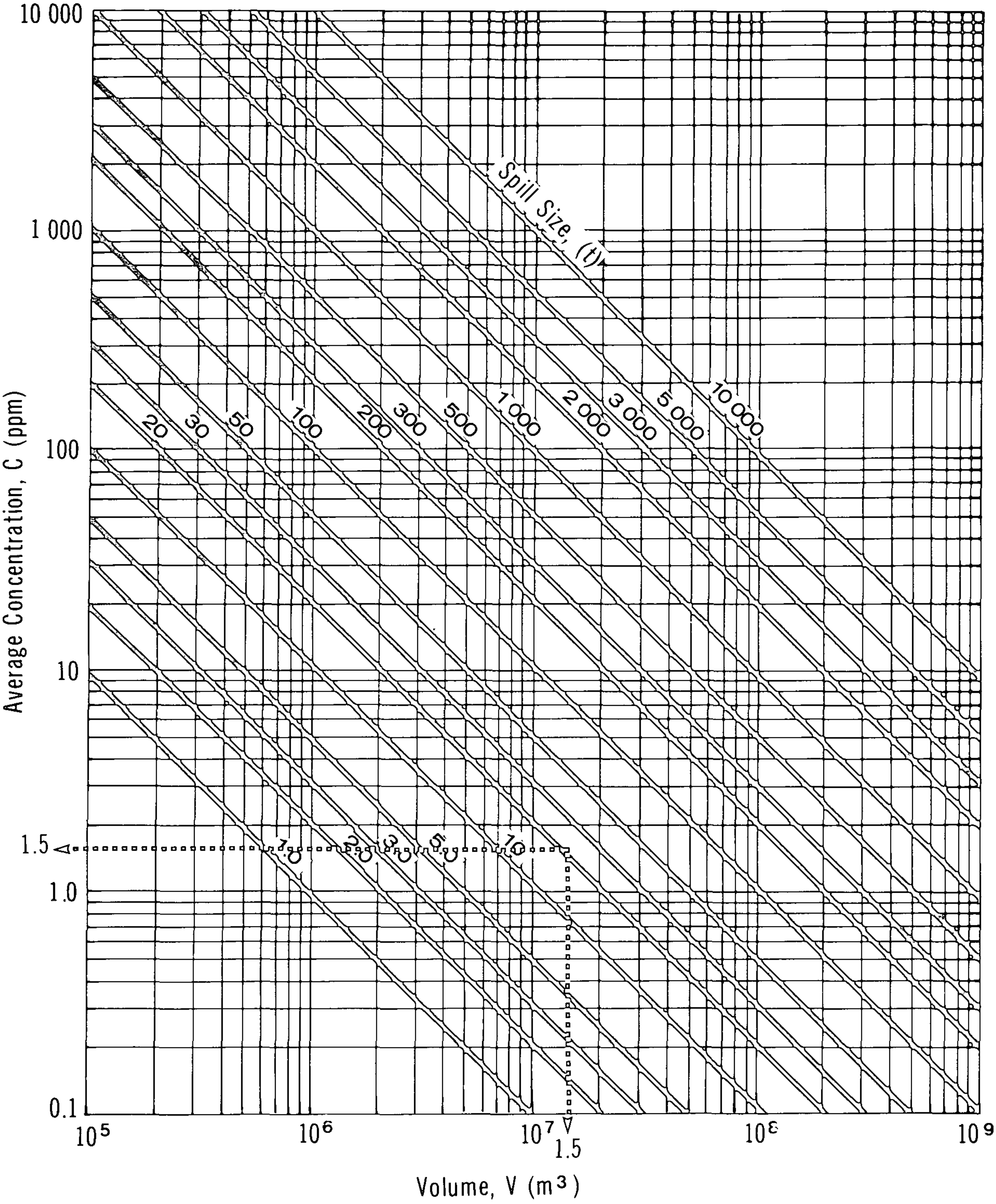
Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s
- spill mass = 20 tonnes
- X = 5000 m

Step 2: Calculate time to reach point of interest

- Use Figure 29
- With X = 5000 m and U = 1 m/s, t = 83 min

AVERAGE CONCENTRATION vs VOLUME



Step 3: Calculate hydraulic radius (r)

- Use Figure 30
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate longitudinal diffusion coefficient (E)

- Use Figure 31
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 32
- With E = 69 m^2/s and t = 83 min, α = 2000

Step 6: Calculate delta

- Use Figure 33
- With alpha (α) = 2000 and spill mass = 20 tonnes, delta (Δ) = 10

Step 7: Compute stream cross-sectional area (A)

- A = W x d = 50 x 5 = 250 m^2

Step 8: Calculate maximum concentration (C) at point of interest

- Use Figure 34
- With Δ = 10 and A = 250 m^2, C = 40 ppm

5.4.5.3 **Average pollutant concentration in lakes or still water bodies.** A 20 tonne spill of ammonia has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1000 m
- spill mass = 20 tonnes

Step 2: Determine the volume of water available for dilution

- Use Figure 35
- With r = 1000 m, d = 5 m, the volume is approximately 1.5 x 10^7 m^3

Step 3: Determine the average concentration

- Use Figure 36
- With V = 1.5 x 10^7 m^3 and spill mass = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soils and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of anhydrous ammonia onto soil and its subsequent subsurface transport are presented here.

Anhydrous ammonia has a boiling point of -33.4°C at atmospheric pressure. Consequently, when it is spilled onto a soil surface, extensive evaporation will occur initially. Data presented in Section 5.3 of this manual indicate an initial evaporation rate from a pool of anhydrous ammonia of 16.4 $g/(m^2 \cdot s)$ at 20°C. Ammonia entering the soil will continue to evaporate but at a reduced rate. Thus, only limited amounts of ammonia will remain for transport down through the soil toward the groundwater table. The analysis used in this section assumes that some ammonia does remain for downward transport.

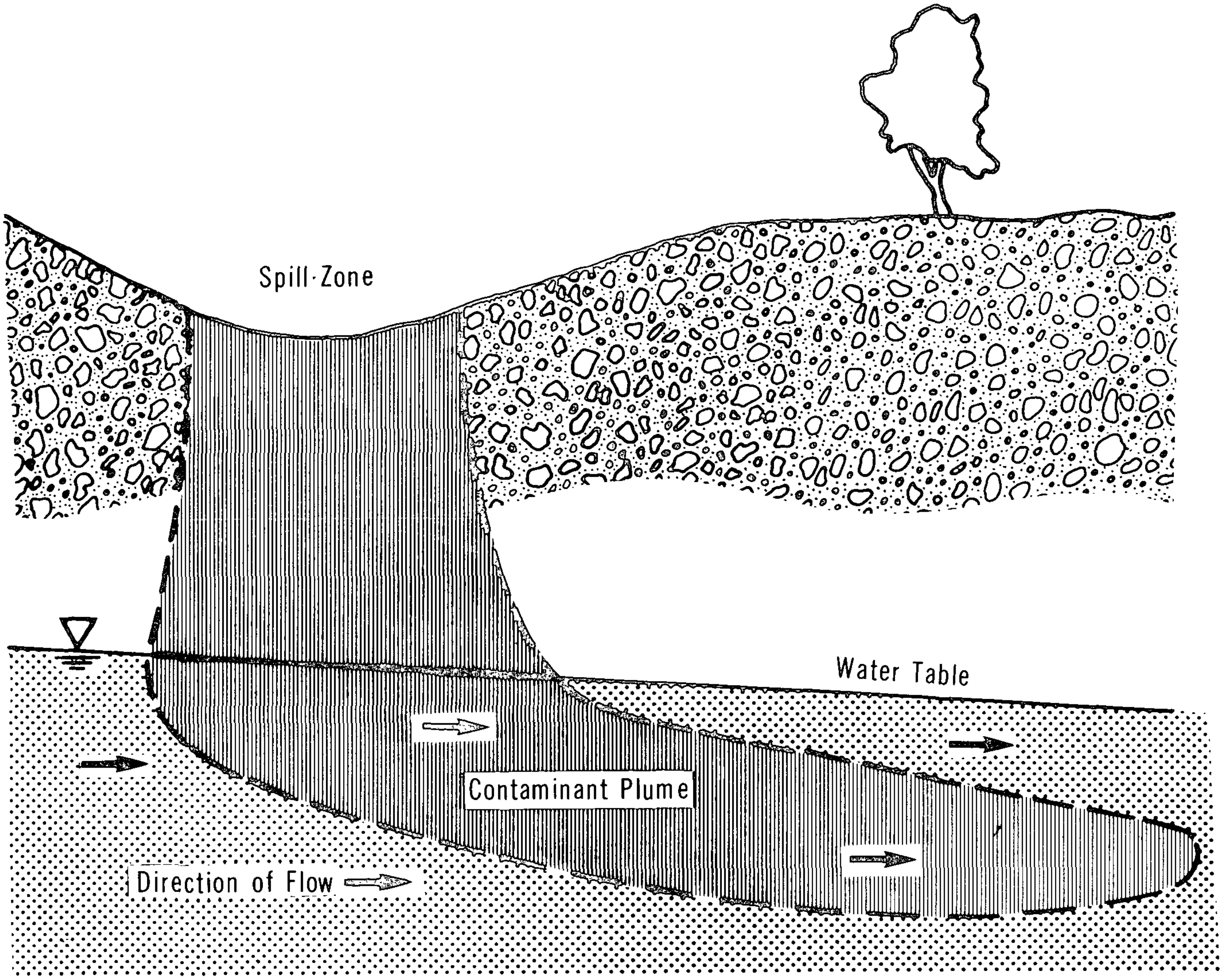
Since ammonia is miscible with water, the moisture regime in the soil at the time of the spill is important. If the soil surface is at or near saturation, spilled ammonia will be slow to penetrate the soil and will run off and/or evaporate. If the soil is not saturated with water, ammonia penetration will occur. The worst case will occur when the soil is at field capacity with respect to water. In this case, the ammonia will penetrate the soil and continue to move downward, with only small amounts remaining as a part of the interstitial fluid. Moisture present in the soil or added as precipitation at the time of the spill will dilute the ammonia, thus reducing its rate of evaporation.

When the ammonia reaches the saturated groundwater table, it will continue to move in the direction of groundwater flow and will be diluted slowly through diffusion. A plume of contamination in the direction of flow will be produced within the groundwater system. The ammonia concentration will be reduced from the initial value, particularly at the edges of the plume. This is shown schematically in Figure 37.

Ammonia is known to adsorb onto soils, particularly those containing clay minerals. However, this is reversible adsorption, such that subsequent infiltration of water will cause the ammonia to desorb. The result will be a retardation of the ammonia transport rate.

5.5.2 Equations Describing Ammonia Movement in Soil. The assumptions and simplifications used to describe contaminant movement downward through the unsaturated soil layers and toward the groundwater table have been described in the Introduction

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Anhydrous Ammonia. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

where:
k = intrinsic permeability of the soil (m^2)
ρ = mass density of the fluid (kg/m^3)
μ = absolute viscosity of the fluid (Pa•s)
g = acceleration due to gravity = 9.81 m/s^2

Property	Anhydrous Ammonia		Water
	20°C	4°C	20°C
Mass density (ρ), kg/m^3	610	640	998
Absolute viscosity (μ), Pa•s	0.15×10^{-3}	0.18×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(4.0 \times 10^7)k$	$(3.5 \times 10^7)k$	$(0.98 \times 10^7)k$

5.5.4 Soils. The Introduction Manual describes the three soils chosen for this work. Their relevant properties are:

	Soil Type		
	Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (Θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of anhydrous ammonia into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against penetration depth (B). It is assumed that some ammonia will eventually reach the groundwater table. Because of the methods used in the calculation, the penetration depth obtained from the nomograms is the maximum value to be expected in time t_p.

A flowchart for the use of the nomograms is presented in Figure 38. The nomograms are presented as Figures 39, 40 and 41.

The water line on each nomogram shows the rate of penetration of water at 20°C. It represents a lower limit to the rate of ammonia penetration, should it become diluted with water.

5.5.6 Sample Calculation A 20 tonne spill of ammonia has occurred on coarse sandy soil. The ammonia temperature is 4°C; the spill radius is 8.6 m. Calculate the depth of penetration and check the corresponding evaporation loss.

Solution

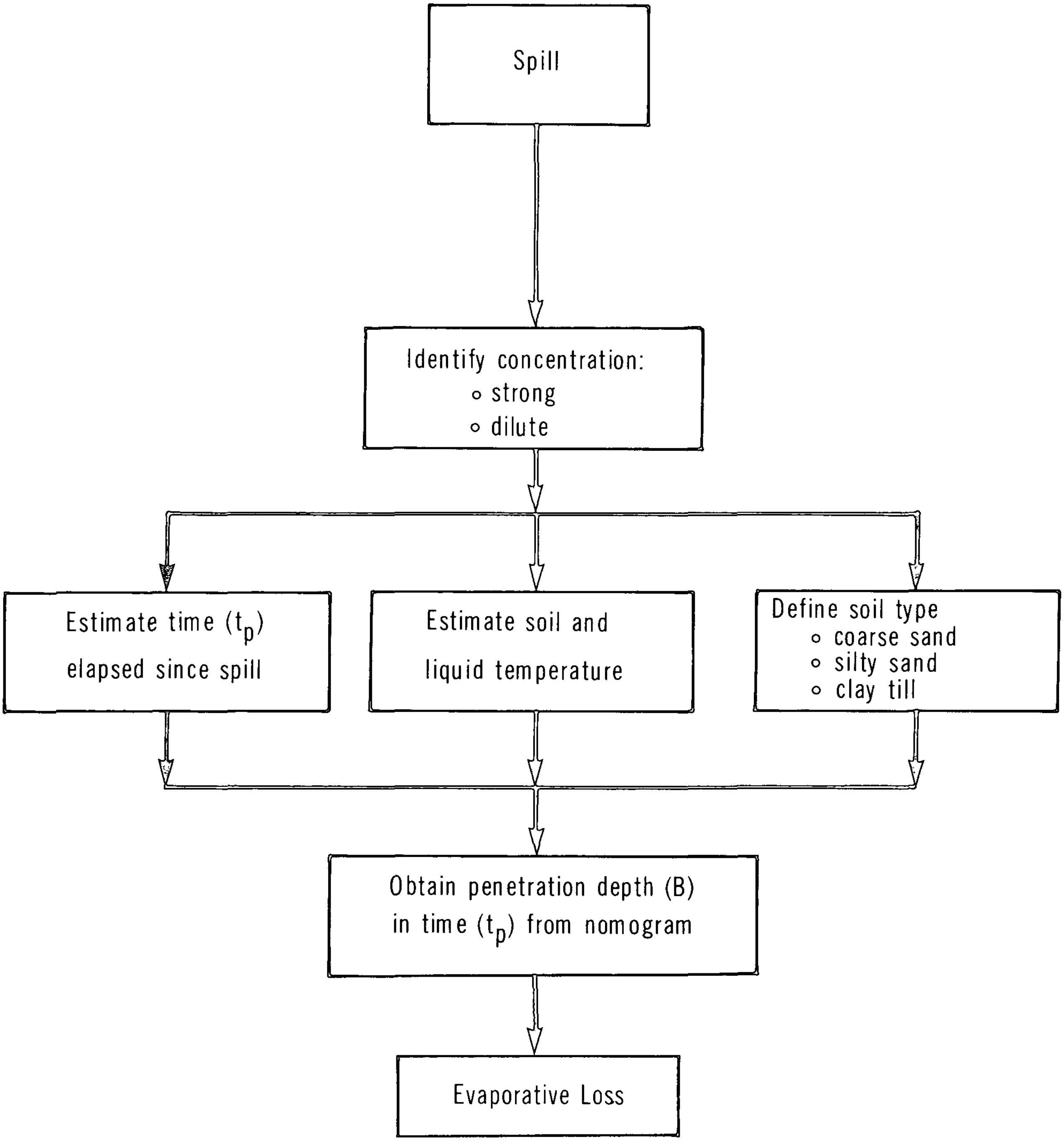
Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- $T = 4°C$
- $r = 8.6$ m
- $A = \pi r^2 = 232\ m^2$
- Time elapsed since spill (t_p) = 5 min

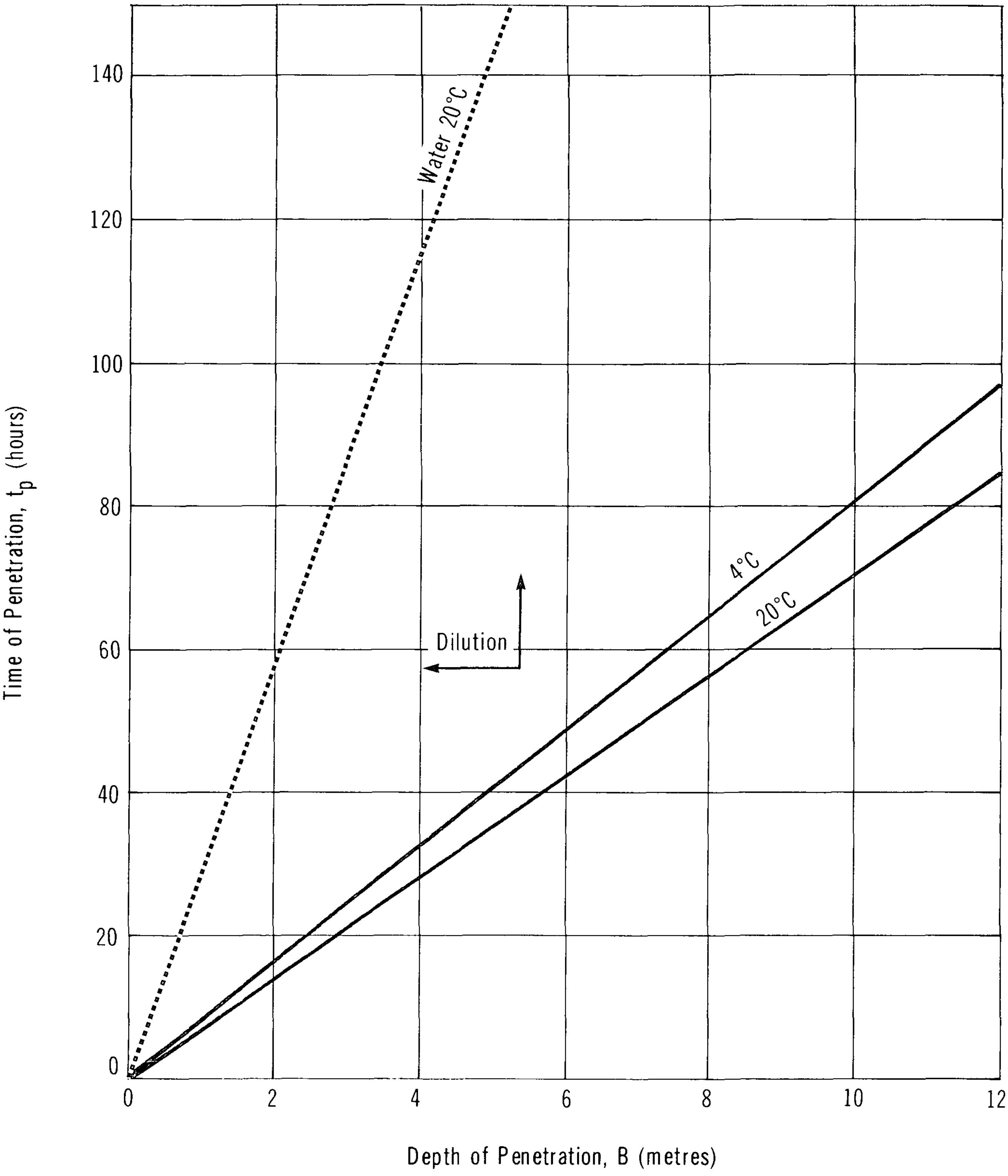
Step 2: Estimate depth of penetration (B)

- For coarse sand, B = 10.5 m as maximum depth of penetration in t_p = 5 min

FLOWCHART FOR NOMOGRAM USE



PENETRATION IN SILTY SAND



PENETRATION IN COARSE SAND

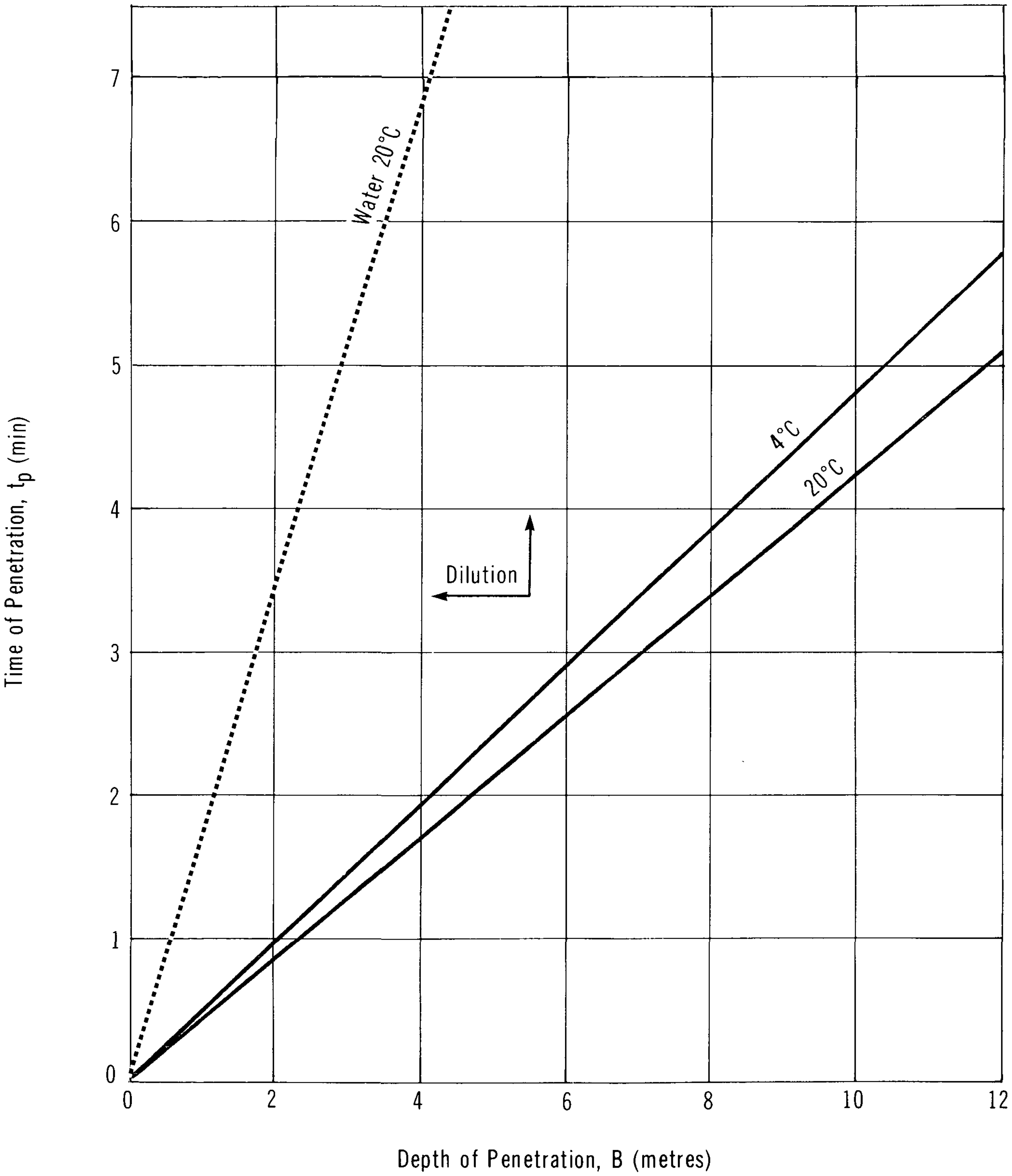
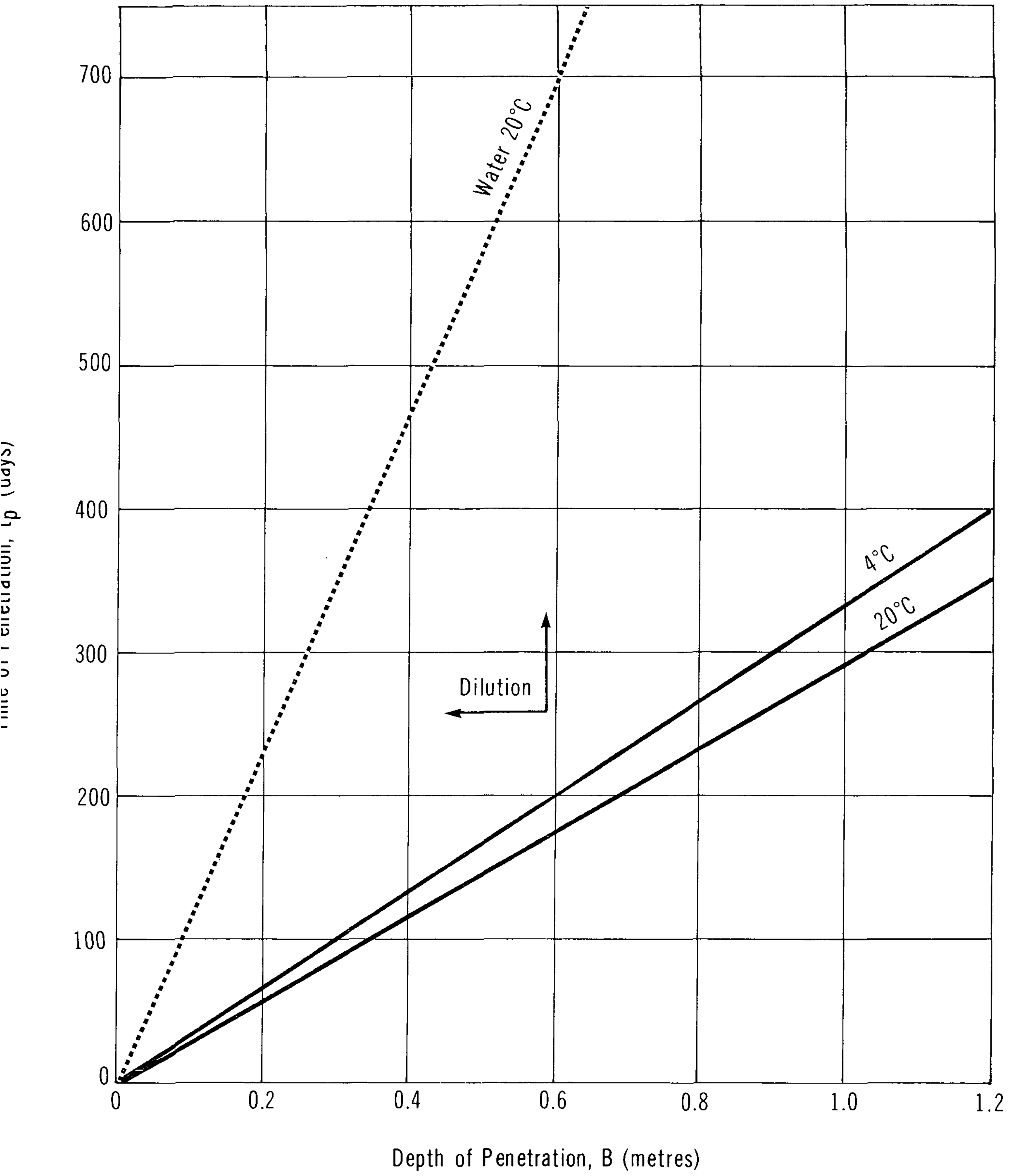


FIGURE 41

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Canada.

6.1.1.1 Water. The maximum acceptable level of ammonia in water for domestic consumption is 0.5 mg/L. The objective level is 0.01 mg/L (WQS 1979).

Alberta, Saskatchewan, Manitoba, New Brunswick, Newfoundland and Nova Scotia follow the Federal Government recommendations of 0.05 ppm ammonia in water for human consumption and 1.0 ppm ammonia for body contact (O.I. 1970).

6.1.1.2 Air. Ontario's limit for the emission of ammonia is 3.6 mg/m^3 (Ontario E.P. Act 1971). Alberta's emission guideline for new plants is 1.5 kg/t of ammonia produced; the objective level is a rate of 1.0 kg/t (Ammonia 1979).

6.1.2 Others.

6.1.2.1 Water. The water quality criteria for ammonia developed for the protection of aquatic life and human health in the United States are presented in Table 12 (API 1981).

The maximum allowable concentrations (M.A.C.) for ionized ammonia (NH_4^+) in surface waters in Bulgaria and Poland are the following (Verschueren 1977):

Class	Bulgaria (1976) NH_4^+ (mg/L)	Poland (1975) NH_4^+ (mg/L)
I	0.05	1.0
II	0.1	3.0
III	3.0	6.0

6.2 Aquatic Toxicity

6.2.1 Canadian Toxicity Rating. Ontario recommends that the unionized ammonia (NH_3) concentration for aquatic life protection should not exceed 0.02 mg/L (Water Management Goals 1978).

6.2.2 U.S. Toxicity Rating. Ammonia has been assigned a TL_m 96 (4-day median lethal toxicity rating) of 1 to 10 mg/L. Ammonium hydroxide has a TL_m 96 of 10 to 100 mg/L (RTECS 1979).

TABLE 12 WATER QUALITY CRITERIA

Water Use	Criteria	Criteria Support Data	Reference
Aquatic life	Case-by-case flow-through bioassay	Tests should be conducted at pH 8.5 and DO[1] of 4-5 mg/L	Green Book FWPCA 1968. IN API 1981
	0.02 mg/L as unionized ammonia (NH_3) (upper limit at any time or place) or 0.05 x 96 hour LC_{50}, but no higher than 0.02 mg/L	(0.5 of a physiological effect level for rainbow trout) 0.05 as a conservative factor	Blue Book NAS 1973. IN API 1981
	0.02 mg/L as unionized ammonia (NH_3)	0.1 x 0.2 mg/L, value for rainbow trout	Red Book EPA 1976. IN API 1981
Public Water Supply	0.5 mg/L as (N) permissible	Ammonia can react with free chlorine to decrease effectiveness of disinfection	Green Book FWPCA 1968. IN API 1981
	0.5 mg/L PWS	Cites Green Book (normal surface waters are $\leq$0.1 mg/L	Blue Book NAS 1973. IN API 1981
	No PWS std	-	Red Book EPA 1976. IN API 1981
Livestock	170 mg/L ammonia	-	OHM-EPEW 1968

[1] DO = dissolved oxygen

6.2.2.1 Recommendations for freshwater aquatic life. Two options were recommended for ammonia criteria: 1) a maximum value of 0.02 mg/L of unionized ammonia (NH_3) or 2) a numerical value derived by multiplying a 96-h LC_{50} value times the application factor of 0.05. In either case, the numerical criterion is to be no higher than 0.02 mg/L of unionized ammonia. This value is recommended by the National Academy of Sciences (Blue Book 1973. IN API 1981) and the Environmental Protection Agency (Red Book 1976. IN API 1981).

The criterion (Red Book 1976. IN API 1981) of 0.02 mg/L as unionized ammonia was derived by applying a safety factor of 0.1 to the lowest lethal concentration value of 0.2 mg/L NH_3 for rainbow trout. The latter value was traced to a 1948 reference; upon recomputation using more accurate tables, the effect level was indicated to actually be 0.32 mg/L. It was also pointed out that the appropriateness of the 0.02 mg/L criterion for nonsalmonid freshwater fish or other freshwater aquatic life was not documented. Also, no criteria were proposed for estuarine or marine organisms. EPA took the position that the Red Book criteria have presumptive applicability to all waters, which has greatly influenced the water quality standards of many states. The above is presented as a critique of the recommended criteria (API 1981).

6.2.2.2 Recommendations for marine aquatic life. On the basis of freshwater data available, it is suggested that concentrations of unionized ammonia equal to or exceeding 0.4 mg/L constitute a hazard to the marine biota, and levels less than 0.01 mg/L present minimal risk of deleterious effects. An application factor of 0.1 should be applied to marine 96-h LC_{50} data for the appropriate organisms most sensitive to ammonia (WQC 1972).

6.2.3 Measured Toxicities.

6.2.3.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Water Result	Conditions	Reference
Fish Toxicity Tests					
34.4 (total NH_3-N)	96	Rainbow trout	LC_{50}	hard, 13°C, pH 7.87	Thurston 1981

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
47.1 (total NH_3-N)	96	Fathead minnow	LC_{50}	hard, 11.8°C, pH 7.83	Thurston 1981
270 (total NH_3-N)	24	Channel catfish	LC_{50}	20-24°C, pH 6.9 -7.1	Spehar 1981
1.39 to 1.82	24	Channel catfish	LC_{50}	21-25°C, pH 7-9	Tomasso 1980
0.47 to 0.5 (unionized NH_3)	24	Rainbow trout	LC_{50}		Ammonia 1979
0.068 (unionized NH_3)	24	Rainbow trout fry (85 days old)	TL_m	10°C, pH 8.3	Ammonia 1979
0.097 (unionized NH_3)	24	Rainbow trout (adult)	TL_m	10°C, pH 8.3	Ammonia 1979
1.1658 (unionized NH_3)	96	Bluegill	LC_{50}	24°C, pH 8.6	Hazel 1979
0.42 (unionized NH_3)	24	Roach *(Rutilus rutilus)*	LC_{50}		Ammonia 1979
0.74 to 0.88	96	Orange throat darter *(Etheostoma spectabile)*	LC_{50}	21-22°C, pH 8.4	Hazel 1979
2.33 to 2.60 (unionized NH_3)	96	Red shiner *(Notropis lutrensis)*	LC_{50}	24°C, pH 8.2-9.2	Hazel 1979
0.99 (unionized NH_3)	96	Red shiner	LC_{50}	26.5°C, pH 7.7-8.5	Rosage 1979
0.5 to 0.8 (unionized NH_3)	96	Cutthroat trout fry (1 to 3 g)	LC_{50}	flow-through bioassay	Thurston 1978
0.34 (unionized NH_3)	29 days	Tissues of cutthroat trout fry	degenerative changes in gills, kidneys and liver	flow-through bioassay	Thurston 1978

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
1.6 (unionized MH_3)	96	Channel catfish	LC_{50}	27.9°C, pH 8.30-8.44	Colt 1978
0.72; 1.2 (NH_3-N)	96	Bass	TL_{50}	22°C; 30°C high alkalinity, lake water (Illinois)	Roseboom 1977
0.66 to 2.62 (unionized NH_3)	24	Guppy fry *(Poecilia reticulata)*	LC_{50}	25°C, pH 7.9-8.5	Rubin 1977
1.06 to 1.38 (unionized NH_3)	48	Guppy fry	LC_{50}	25°C, pH 7.9-8.5	Rubin 1977
1.00 to 1.26 (unionized NH_3)	96	Guppy fry	LC_{50}	25°C, pH 7.9-8.5	Rubin 1977
0.51 (unionized NH_3)	4	Coho salmon fingerlings *(Oncorhynchus kisutch)*	LC_{50}	14.7-19.7°C, pH 7.1-9.1	Buckley 1978
0.45 (unionized NH_3	96	Coho salmon fingerlings	LC_{50}	14.7-19.7°C, pH 7.1-9.1	Buckley 1978
0.432 to 0.664 (unionized NH_3)	96	Cutthroat trout *(Salmo clarki)*	LC_{50}	11.7-12.4°C, pH 7.7-7.93	Thurston 1978
0.227 to 0.589 (unionized NH_3)	96	Coho salmon fingerlings	LC_{50}	15°C, pH 7.0-8.0	Robinson-Wilson 1975
0.4; 1.3 (NH_3-N)	96	Bluegill (*Lepomis macrochirus*)	TL_{50}; temp. & fish wt. dependent	22°C; 30°C high alkalinity, lake water (Illinois)	Roseboom 1977
1.5; 3.0 (NH_3-N)	96	Channel catfish	TL_{50}	22°C; 28°C, high alkalinity, lake water (Illinois)	Roseboom 1977
2.36 (unionized NH_3)	24	Channel catfish	LC_{50}	25°C, pH 8.5-8.9	Robinette 1976

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
2.4 to 3.8 (unionized NH$_3$)	96	Channel catfish (*Ictalurus punctatus)*	LC$_{50}$	22-30°C, pH 8.6-8.8	Colt 1976
0.14 to 0.5	24	Atlantic salmon smolt	LC$_{50}$		WQCEFF 1973
1.004 (unionized MH$_3$)	96	Green sunfish (*Lepomis cyanelles)*	LC$_{50}$	12.0-12.6°C, pH 7.72-8.0	Jude 1973
0.2837 (unionized NH$_3$)	66	Pumpkinseed (*Lepomis gibbosus)*	LC$_{50}$	11.7-12.3°C, pH 7.55-7.9	Jude 1973
5 to 8	not stated	Coho salmon	loss of equilibrium spasms with gills & jaws gaping	aerated	WQC 1972
510 (NH$_4$Cl)	48	Mosquito fish	LC$_{50}$	high turbidity	WQC 1972
0.29 (unionized NH$_3$)	7 days	Perch	LC$_{50}$		WQC 1972
161 (NH$_4$Cl)	48	Crucian carp	LC$_{50}$	std. ref. water	WQC 1972
0.04 N	not stated	Threespine stickleback	immediate negative response		WQC 1972
0.41 (unionized NH$_3$)	24	Bream (*Abramis brama)*	LC$_{50}$	9.4-14.6°C, pH 7.75-8.12	Ball 1967
0.50 to 0.61 (unionized)	48	Rainbow trout *(Salmo gairdneri)*	LC$_{50}$	17.5-17.7°C, pH 6.9-7.8	Herbert 1964
0.32 to 0.35	24	Rainbow trout	LC$_{50}$	13.6°C, pH 7.51-7.52	Herbert 1964
3.4	96	Bluegill	TL$_m$	soft, 20°C	WQC 1963
24.4	96	Bluegill	TL$_m$	hard, 20°C	WQC 1963
Fish Kill Data					
0.44 (unionized NH$_3$)	3	Rainbow trout	100% mortality	10.5°C, pH 8-10	WQC 1972

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
5 to 7 ppm (unionized NH_3)	6	Minnows	toxic or lethal	distilled, 20°C	WQC 1963
5.0 (unionized NH_3)	24	Brown bullhead *(Ictalurus nebulosus)*	100% mortality	26°C, pH 7.8	Robbins 1977
4.1 (unionized NH_3)	3	Bluegill	100% mortality	27°C, pH 8.4	Robbins 1977
6.5 (unionized NH_3)	48	Largemouth bass (*Micropterus salmoides)*	100% mortality	26°C, pH 7.9	Robbins 1977
3.1 (unionized NH_3)	3	Spotfin shiner (*Notropis spilopterus)*	100% mortality	26.5°C, pH 7.9	Peterson 1977
2.0 (unionized NH_3)	18	Spotfin shiner	100% mortality	26.5°C, pH 8.1	Peterson 1977
Microorganisms					
0.66	48	*Daphnia magna*	LC_{50}	22°C, 30°C	WQCEFF 1973
8	not stated	Daphnia	lethal		WQC 1963
420	120	Diatom	TL_m, 50% growth reduction	hard, 22°C soft, 22°C	WQC 1963
75 to 86	not stated	Copepod (cyclops)	threshold of immobilization		WQC 1972
17	not stated	Green algae	inhibition of growth		WQC 1972
3.1	not stated	Water flea	threshold of immobilization		WQC 1972
28.8 (anhydrous)	24	Zooplankton, phytoplankton	reduced by 99%, 96% respectively	pond, pH 6.9 (surface area 1.78 ha)	Ammonia 1979

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Invertebrates</u>					
90	96	Snail	TL_m	soft, 20°C	WQC 1972
28.8 (anhydrous)	24	Crayfish, shrimp	lethal	pond (surface area of 1.78 ha) pH 6.9	Ammonia 1979
1.72 to 2.94 (unionized NH_3)	24	Freshwater prawn *(Macrobrachium rosenbergii)*	LC_{50}	28°C, pH 7.6-8.34	Armstrong 1978
0.54	24	Freshwater prawn	LC_{50}	28°C, pH 6.83	Armstrong 1978
0.66 to 1.11 (unionized NH_3)	144	Freshwater prawn	LC_{50}	28°C, pH 7.6-8.34	Armstrong 1978
2.81 (unionized NH_3)	9	Freshwater prawn	LC_{50}	29.2°C, pH 7.0	Wickens 1978
3.2 (unionized NH_3)	24	Crayfish *(Orconectes nais)*	LC_{50}	28°C, pH 8.5	Hazel 1979
3.15 (unionized NH_3)	24	Crayfish	LC_{50}	26-27°C, pH 8.0	Evans 1979
<u>Aquatic Vegetation</u>					
28.8 (anhydrous)	24	Rooted vascular plants	complete eradica-cation	pond (surface area of 1.78 ha), pH 6.9	Ammonia 1979
3 (NH_3 in air)	24	Aquatic plants	injury		Yopp 1974
<u>Vertebrates</u>					
28.8 (anhydrous NH_3)	24	Frogs, tadpoles	lethal	pond (surface area of 1.78 ha), pH 6.9	Ammonia 1979

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Euryhaline Species					
0.04 to 0.23 (union-ized NH_3)	24	Atlantic salmon (*Salmo salar*)	LC_{50}	12°C, pH 7.66-8.01	Alabaster 1979
0.15 to 2.13	96	White perch (*Morone americana*)	LC_{50}	16°C, pH 6-8	Stevenson 1977
0.71 to 0.84	96	Threespine stickleback (*Gasterosteus aculeatus*)	LC_{50}	15-23°C, pH 6.8-7.3	Hazel 1971

6.2.3.2 Saltwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxicity Tests					
0.11 (unionized NH_3)	62 days	Sockeye salmon eggs	LC_{50}	10°C, pH 8.4	Spehar 1981
0.36 to 0.42 (unionized NH_3)	24	Porgy larvae (*Diplodus sargus*)	LC_{50}	15°C, pH 7.85	Brownell 1980
0.46	24	Cod (*Gaidropsarus capensis*)	LC_{50}	15°C, pH 7.85	Brownell 1980
0.76 to 1.2 (unionized NH_3)	96	Striped bass (*Morone saxatilis*)	LC_{50}	15-23°C, pH 7.3-8.0	Hazel 1971
0.97; 0.73 (unionized NH_3)	96	Striped bass	TL_m	15°C; 23°C	Ammonia 1979
5.05; 1.12 (unionized NH_3)	96	Stickleback	TL_m	15°C; 23°C	Ammonia 1979

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.65 to 0.7 M (total NH_3)	not stated	Shark	reduced serum protein; caused skin lesions	recirculating water	Ammonia 1979
3.5 to 10	not stated	Chinook salmon	reduction in growth; loss of equilibrium	aerated	WQC 1972
Invertebrates					
8.36 to 23.46 (unionized NH_3)	96	American oyster (*Crassostrea virginica*)	LC_{50}	20°C, pH 7.7-7.96	Epifanio 1975
3.06 to 4.49	96	Quahog clam (*Mercenaria mercenaria*)	LC_{50}	20°C, pH 7.7-7.96	Epifanio 1975
0.22 to 0.69	3 weeks	Various shrimp species	EC_{50}	28°C	Wickins 1976
1.29	48	Various shrimp species including *Penaeus aetecus*, *P. japonicus*, *P. orientalas*, *P. schmitti*, *P. setiferus*	LC_{50}	28°C	Wickins 1976
6.2	48	Green mussel (*Perna viridis*)	LC_{50}	28-30°C, pH 8.7-8.85	Reddy 1979
11.6	96	Green mussel	LC_{50}	28-30°C, pH 8.7-8.85	Reddy 1979

6.2.4 Aquatic Studies.

6.2.4.1 Fish. The general conclusion regarding the toxic action of ammonia to fish is still not clear; additional research is required. Research over the years has, however, supported the hypothesis that the unionized molecule (NH_3) is the primary toxic form and that the ionized species (NH_4^+) is considerably less toxic. This is presumably because the electrically neutral unionized form is lipid-soluble and apparently requires no energy-dependent active transport mechanism to pass through cell membranes and affect the organisms internally. In contrast, the more prevalent ionized form (NH_4^+) is unable to pass through the charge-lined micropores of the hydrophobic membrane components. Some typical conclusions from studies are presented in the next paragraph.

It was concluded that the minor histopathological changes to gill structure produced by acutely lethal concentrations of ammonia appeared unlikely to have significantly impaired oxygen uptake. It was suggested that exposure to ammonia reduces the pH of the fish blood, resulting in a negative effect on the oxygen transport function of the hemoglobin molecule. Other evidence demonstrated that the permeability of fish to water is increased by exposure to ammonia; it was thus concluded that death probably occurs when the increase in permeability exceeds the maximum sustained urine production rate. Other authors refute this hypothesis because the hydromineral imbalance in exposed rainbow trout, combined with the absence of changes in plasma and tissue chloride levels of channel catfish, seem to exclude this osmoregulatory disruption theory. It was also suggested that the toxicity of ammonia may depend in part on the Na^+/NH_4^+ ratio. Finally, it was suggested that the acute toxic action of unionized ammonia to fish may involve the impairment of cerebral energy metabolism, resulting in the depletion of essentially high energy compounds to the brain. This same toxic mechanism has been proposed for mammals (API 1981).

6.2.4.2 Plants. Disagreement has arisen in various studies as to whether lake plants grow better with nitrate or ammonia as a nitrogen source. There is evidence of phytoplankton blooms during which sudden decreases in ammonia occurred with little decrease in nitrate concentration. Another study showed that algal nitrate uptake, but not growth, was inhibited by ammonia in Sanctuary Lake, Pennsylvania (Ammonia 1979).

6.3 Toxicity to Other Biota

6.3.1 Avian.

Conc. (mg/m^3)	Time (hours)	Species	Result	Reference
1600 (enclosed building)	7 min	Starlings, sparrows, pigeons	death	Ammonia 1979

6.3.2 Mammals.

Conc. (mg/m^3)	Species	Result	Reference
59.8 to 1302.4	Bats	no adverse physiologic effects	Ammonia 1979
2112	California leaf-nosed bat	death after 1 to 9 h elapsed exposure time	Ammonia 1979
4928	Mexican free-tailed bat	death after 2 to 3 h elapsed exposure time	Ammonia 1979

6.3.3 Livestock.

Conc. (mg/m^3)	Species	Result	Reference
14.1 to 35.2	Poultry	reduced feed consumption, reduced weight gain, airsacculitis, increased susceptibility to respiratory diseases, general discomfort	Ammonia 1979
42.2 to 70.4	Poultry	reduced egg production, tracheitis, and keratoconjunctivitis (ocular disorder)	Ammonia 1979
>70.4	Swine	reduced growth rate	Ammonia 1979
70.4 to 105.6 (5 wk)	Pigs	excessive nasal, lacrimal and mouth secretions	Ammonia 1979
not specified (NH_3 gas + other manure gases)	Cattle (calves)	reduced growth rate, death (in confined units)	Ammonia 1979
7 to 1408	Cattle (dairy) (calves)	high morbidity and mortality rates	Ammonia 1979

6.3.4 Plants.

Conc. (mg/m^3)	Time (hours)	Species	Result	Reference
176	4 min	Tomato	50% foliar necrosis	Ammonia 1979
704	5 min	Buckwheat	50% foliar injury	Ammonia 1979
704	8 min	Tobacco	50% foliar injury	Ammonia 1979
28.2	1	Tomato, sunflower	injured plants	Ammonia 1979
28.2	1	Coleus	leaf colour lost	Ammonia 1979
2.1	4	Mustard weed	severely injured	Ammonia 1979
8.4	4	Pigweed, goosefoot	slightly injured	Ammonia 1979
140.8	not stated	Peach fruit	developed temporary overall darkening of skin	Ammonia 1979
>282	not stated	Apples	developed permanent dark discolouration around lenticels	Ammonia 1979
704	16	Radish seeds	killed	Ammonia 1979
704	4	Spring rye seeds	killed	Ammonia 1979
176	16	Spring rye seeds	reduced germination by 52%	Ammonia 1979
not stated	not stated	Onions	discolouration of outer skins, immediately after exposure	Ammonia 1979

Conc. (mg/m^3) (gas)	Leaf Uptake Rate (mg/m^2)/h	Species	Result	Reference
0.024	0.40	Soybean	foliar absorption and assimilation of NH_3	Ammonia 1979

Conc. (mg/m^3) (gas)	Leaf Uptake Rate (mg/m^2)/h	Species	Result	Reference
0.031	0.49	Sunflower	foliar absorption and assimilation of NH_3	Ammonia 1979
0.024	0.56	Corn	foliar absorption and assimilation of NH_3	Ammonia 1979
0.044	0.35	Cotton	foliar absorption and assimilation of NH_3	Ammonia 1979
0.7 to 14	not stated	Corn seedlings	foliar absorption and assimilation of NH_3	Ammonia 1979

6.3.4.1 Plant studies (Ammonia 1979). Plants have a high affinity for gaseous ammonia when leaf stomata are open in daylight. Various species of plants are known to accumulate nitrate. Accumulation results from uptake of nitrate in excess of the capacity to reduce and assimilate it.

Foliar injury symptoms on broad-leaved woody plants exposed to high concentrations of ammonia usually begin as large, dark green, water-soaked areas that darken after several hours into brownish-gray or black necrotic lesions, which are widely scattered over the leaf surface. On trees or shrubs with crowded or overlapping leaves, injury may be confined to particular sections of the leaf. Foliar lesions can occasionally turn orange, purple, or reddish-brown, mimicking fall colouration.

Conifer foliage injured by exposure to ammonia darkens to shades of gray-brown, purple, or black. The entire part of the needle exposed to the gas is usually affected.

Symptoms of injury are more variable on herbaceous plants than on woody species, ranging from irregular, bleached, bifacial, necrotic lesions to reddish interveinal streaking or dark upper-surface discolouration.

6.4 Effect Studies

Fish studies have shown that the toxicity of ammonia (in terms of NH_3) increases at lower pH values (Thurston 1981). It is concluded that NH_4^+ exerts some measure of toxicity and/or that increased H^+ concentration increases the toxicity of NH_3. It is recommended that water quality criteria be revised to consider the pH dependence of the toxicity of ammonia (Thurston 1981). The principal effect of pH is on the dissociation of ammonia into its two primary aquatic fractions, the recognized toxic unionized form and the predominant and relatively nontoxic ionized form:

$$NH_3 + H_2O \underset{2}{\overset{1}{\rightleftarrows}} NH_4^+ + OH^- \qquad \begin{array}{l} (1) > (2) \text{ with decreasing pH} \\ (2) > (1) \text{ with increasing pH} \end{array}$$

The concentration of unionized ammonia increases approximately tenfold with an increase in pH from 7 to 8 at 20°C. Many researchers, however, have indicated the effect of pH cannot be explained solely by its effect on the percentage of unionized ammonia in solution. One author, for example, reported that a decrease in pH from 8.0 to 6.0 would theoretically result in a 97-fold decrease in unionized ammonia; however, the observed toxicity reduction to white perch was only decreased by factors of 29 and 9 in fresh and brackish water, respectively. Other results indicated that although the concentration of (total) ammonia yielding the 96-hour LC_{50} decreased as pH increased, in terms of unionized ammonia the toxicity decreased as pH increased. This same trend was reported using crustacean larvae. The acute toxicity of unionized ammonia (NH_3) varied inversely with pH while the toxicity of ionized ammonia (and total ammonia) varied directly with pH (API 1981):

- NH_3 toxicity increases with decreasing pH.
- NH_4^+ (and total ammonia) increases with increasing pH.

Several laboratory experiments of relatively short duration have shown that the lethal concentration of ammonia for a variety of fish species is 0.2 to 2.0 mg/L. Rainbow trout appear to be the most sensitive and carp the most resistant to aqueous ammonia (Ammonia 1979). The table shown below somewhat verifies the above statement:

96-h LC_{50} VALUES, BY FAMILY$^{(a)}$ (mg/L NH_3-N) (API 1981)

Family	Mean	Range	n
Salmonidae (trouts)	0.493	0.227 - 0.664	9
Percidae (perches)	0.814	0.743 - 0.884	2
Percichthyidae (temperate basses)	0.827	0.15 - 2.13	6
Antrarchidae (sunfishes)	0.901	0.284 - 1.65	10
Poeciliidae (livebearers)	1.28	0.58 - 2.27$^{(b)}$	2

Family	Mean	Range	n
Cyprinidae (minnows and carps)	1.55	0.30 - 2.60	6
Gasterosteidae (sticklebacks)	1.61	0.71 - 4.14	6
Ictaluridae (freshwater catfishes)	2.53	1.5 - 3.8	6

(a) The reported means and ranges incorporate all 96-h LC_{50} values obtained from the literature, regardless of their appropriateness for use in developing water quality criteria, or experimental conditions employed (i.e., pH, temperature, salinity).

(b) Includes calculated NH_3-N concentrations for the entire experimental pH range reported by the authors.

Sublethal exposure to ammonia has been reported to cause adverse physiologic and histopathologic effects in fishes (Ammonia 1979). Studies indicate that concentrations of 1 mg/L decrease the ability of the hemoglobin to combine with oxygen in fish. Ammonia concentrations of 2.5 mg/L in water of pH ranging from 7.4 to 8.5 are considered harmful to fish (Todd 1970).

Due to the slightly higher alkalinity of seawater and the presumably larger concentration of the unionized form, ammonia may be more toxic in seawater than in freshwater (WQC 1972). For given conditions of temperature and measured pH, seawater contains about 40 percent less unionized ammonia than does freshwater. The saline environment has been shown to significantly affect the resistance of certain species to toxic levels of unionized ammonia. It was also demonstrated that the percentage of the toxic unionized ammonia is reduced at increasing salinities. The latter was computed at different temperatures, pHs and ranges of salinities. The toxicity results, however, do not always conform to the values one would expect from the unionized ammonia calculations alone. The following table illustrates the statement above (no cross correlation drawn) (API 1981):

Species	Salinity	pH	Temp. (°C)	96-h LC_{50} (mg/L)
1. White perch	0	6	16	0.15
White perch	14 ppt	6	16	0.20
White perch	0	8	16	0.52
White perch	14	8	16	2.13

Species	Salinity	pH	Temp. (°C)	96-h LC_{50} (mg/L)
2. White perch	0	Unknown	15	1.12
White perch	33%	Unknown	15	1.12
White perch	Full strength seawater	Unknown	15	0.80
White perch	0	Unknown	23	0.76
White perch	33%	Unknown	23	0.84
White perch	Full strength seawater	Unknown	23	0.60
3. Threespine stickleback	0	6.8-7.2	15	0.84
Threespine stickleback	33%	Assumed same	15	5.2
Threespine stickleback	100% seawater	Assumed same	15	10.4
Threespine stickleback	0	7.0-7.3	23	1.8
Threespine stickleback	33%	Assumed same	23	2.4
Threespine stickleback	100% seawater	Assumed same	23	2.3

Resistance	Temp.	pH	Salinity	Species
1. I	C, 16	C, 6	I, 0-14	White perch
I	C, 16	C, 8	I, 0-14	White perch
I	C, 16	I, 6-8	C, 0	White perch
I	C, 16	I, 6-8	C, 14	White perch
I	C, 16	I, 6-8	I, 0-14	White perch
2. C	C, 15	Unknown	I, 0-33	White perch
D	C, 15	Unknown	I, 33-full	White perch
I	C, 23	I, 6-5	I, 0-33	White perch
D	C, 23	I, 6-5	I, 33-full	White perch
D	I	I, 6-5	C, 0	White perch

Resistance	Temp.	pH	Salinity	Species
D	I	I, 6-5	C, 33	White perch
D	I	I, 6-5	C, full	White perch
D	I	I, 6-5	I, 0-33	White perch
D	I	I, 6-5	I, 33-full	White perch
3. I	C, 15	C^{1}, 6.8-7.2	I, 0-33-100	Threespine stickleback
I	C, 23	C^{1}, 7.0-7.3	I, 0-33	Threespine stickleback
D	C, 23	C^{1}, 7.0-7.3	I, 33-100	Threespine stickleback
I	I	$C^{1,2}$	C, 0	Threespine stickleback
D	I	$C^{1,2}$	C, 33	Threespine stickleback
D	I	$C^{1,2}$	C, 100	Threespine stickleback
I	I	$C^{1,2}$	I, 0-33	Threespine stickleback
D	I	$C^{1,2}$	I, 33-100	Threespine stickleback

[1] Assumed change from 6.8-7.2 to 7.0-7.3
[2] Assumed constant for increasing salinity
I = increase
D = decrease
C = constant

6.5 Degradation

6.5.1 Chemical Degradation.

6.5.1.1 Water. Ammonia in water under anaerobic conditions will tend to accumulate, while under aerobic conditions some will be oxidized to nitrate (NO_3^-) (nitrification). Bacteria convert the ammonia first to nitrite (NO_2^-) and then to nitrate, creating an oxygen demand (BOD) in the process. Conversion to nitrite is accomplished by the bacteria largely of the genus *Nitrosomonas* and to nitrate by the genus *Nitrobacter*. The equations for the overall process are:

1) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
2) $NH_4^+ + 1.5O_2 \longrightarrow NO_2^- + H_2O + 2H^+$
3) $NO_2^- + 0.5O_2 \longrightarrow NO_3^-$

Hydroxylamine is formed as an intermediate. Temperature, oxygen supply and pH of the water are factors in determining the rate of oxidation. The optimum pH for nitrification is about 8.5. The conversion process only occurs slowly, if at all, in acidic conditions. The introduction of a large amount of ammonia into a water body will increase the pH of the body according to equation 1 above (Ammonia 1979; API 1981; Kormondy 1969). Other natural processes have been shown to remove ammonia from aquatic systems. These include adsorption to particles of suspended matter, formation of molecular nitrogen through reaction with nitrite (under acidic conditions, pH <5), and loss to the atmosphere across the water-air interface. The rate of the latter process increases with increasing wind speed, temperature, and pH (API 1981).

It is very difficult to generalize about the fate of ammonia discharged to surface waters. The discharge may result from manufacturing processes, dilution water from an emergency response procedure, or a direct spill. The latter, of course, would initially saturate the immediate system and overwhelm many of the natural dissipation processes. Volatilization would surely be the predominant process until dilution was of sufficient magnitude or cleanup reduced the concentration to a level such that the biological processes would predominate. The nitrogen cycle is extremely complex and involves competing biological processes which occur simultaneously in the various microhabitats which comprise aquatic ecosystems, and whose rates depend on such environmental variables as pH, temperature and turbulence. Superimposed on this are the phenomena of volatilization, adsorption and chemical decomposition. Site-specific studies are necessary to understand the fate of ammonia in a given water body (API 1981).

6.5.1.2 Air. Ammonia in neutral or basic solutions will volatilize and escape to the atmosphere. Some of the ammonia in the atmosphere is oxidized to oxides of nitrogen and nitrate ion, which may represent a significant contribution to the total acidity of rainfall (Ammonia 1979).

6.5.2 Biodegradation Rate. The residence time of ammonia in the atmosphere is short (5 to 10 days); the concentration in the troposphere varies widely with location and weather conditions. It is assumed that ammonia combines with sulphate ion in the atmosphere or in washout by rainfall resulting in a rapid return of ammonia to the soil (Ammonia 1979).

6.6 Long-term Fate and Effects

6.6.1 Bioaccumulation and Food Chain Concentration. Ammonia is a naturally occurring compound that does not leave a persistent residue (Ammonia 1979). There is no potential for biological accumulation or food chain contamination (OHM-TADS 1981).

6.6.2 Summary. With few exceptions, the nitrogen of all living organisms is in the ammonia state of oxidation. Thus, the ammonia molecule is essential to life, and the adverse effects of insufficient or excess ammonia represent the extremes of "insufficient" or "excessive" availability of ammonium compounds. Ammonia serves as a nutrient. If ammonia is present in excess, the processes that ultimately funnel it into protein and nucleic acids may become overloaded. Free ammonia may accumulate and cause secondary effects, some of them damaging, either by diverting metabolism in the whole organism or by trapping protons and thereby raising the local pH to damaging values. Ammonia excess can occur either by ammonia spills, accidents, and excessive ammonia in air, soil, or water, or by defective mechanisms for the uptake of ammonia by tissues (i.e., metabolic defects in ammonia uptake by liver, etc.) (Ammonia 1979).

More than 99.5 percent of atmospheric ammonia is produced by natural biological processes. Therefore, ammonia is a "natural" constituent of the troposphere, where it exists in concentrations well below those that are hazardous to humans, animals, and plants (Ammonia 1979).

6.7 Soil

Ammonia is believed to be bound in groundwater samples by the attraction of the positive charge on the ammonium ion to the negatively charged soil micelles. In soil, ammonia is absorbed primarily by four mechanisms - chemically (exchangeable), fixation, reaction with organic matter, and physically. Chemically bound ammonia can generally be removed with a salt solution such as potassium chloride (KCl) and the latter by aeration. Fixed (nonexchangeable) ammonia reacts with soil constituents to give insoluble compounds. Such fixation appears to be associated with clay minerals such as illite and vermiculite. These same materials can also fix exchangeable potassium which reacts with lignin to form complexes. Ammonia's susceptibility to nitrification and, in general, its availability are thus reduced. It has been suggested that the term nonexchangeable be used instead of fixed, since it cannot be extracted by potassium chloride solution.

Reaction with organic matter yields compounds with varying degrees of stability and extractability. These latter materials may require treatment with various acids and/or bases to effect extraction (Hesse 1971; API 1981).

Ammonium ions behave differently under various soil and chemical conditions. Clay soils, for example, hold ammonium ions more efficiently than do sandy soils; soils of low pH bind ammonium ions more efficiently than do soils of high pH. When the cation exchange capacity of the soil is satisfied, such as in a spill condition, the ammonium ions can be leached and transported (API 1981).

6.7.1 Soil Degradation of Material. As noted above, the ammonium ion may be immobile in soil. This will depend on the type of soil, its chemistry, and whether or not its cation exchange capacity has been exceeded. In clay, the positive ion tends to adsorb onto the negative sites of clay colloids. Ammonia may substitute for (exchange with) potassium ion in the lattice structure of a clay mineral or, in reverse, be exchanged by flushing with a potassium salt solution.

The ammonium ion is nitrified (oxidized) by microorganisms to nitrite ion, then to nitrate ion. As nitrate ion, it is more mobile in the soil and can be transported down to the rhizosphere, where it is available for uptake by plants, or through the rhizosphere to groundwater or to local streams or rivers and eventually to the ocean. As noted earlier, ammonium ion may also be transported if the conditions are right.

7 HUMAN HEALTH DATA

Numerous literature reports summarize the human health effects of controlled and accidental acute exposures to ammonia. Overall, the data are adequate to show the irritation effects of ammonia. However, further research is required to identify exposure time and concentration guidelines for spill situations, and to identify long-term health problems associated with acute toxic exposures (PNL 1981). Since 1976, no research projects on the toxicology of ammonia have been reported in the data base TOX TIPS (a summary of current research activity). Limited information is available on the carcinogenic and mutagenic effects of this chemical.

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits

The exposure standards for ammonia are based on its irritant properties. Canadian provincial guidelines are generally similar to those of the American Conference of Governmental Industrial Hygienists (USA-ACGIH) unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV® (8 h)	USA-ACGIH	25 ppm (18 mg/m^3)	TLV 1983
PEL (8 h)	USA-OSHA	50 ppm (35 mg/m^3)	NIOSH/OSHA 1981
	Switzerland	25 ppm (18 mg/m^3)	ILO 1980
	USSR	≃28 ppm (20 mg/m^3)	ILO 1980
	E. Germany	33 ppm (25 mg/m^3)	ILO 1980
	W. Germany	50 ppm (35 mg/m^3)	ILO 1980
Short-term Exposure Limits (STEL)			
STEL	USA-ACGIH	35 ppm (27 mg/m^3)	TLV 1983
Ceiling (5 min)	USA-NIOSH	50 ppm (35 mg/m^3)	NIOSH/OSHA 1981
Other Human Toxicities			
IDLH	USA-NIOSH	500 ppm (350 mg/m^3)	NIOSH Guide 1978
LC_{LO} (5 min)		30 000 ppm	RTECS 1979

Guideline (Time)	Origin	Recommended Level	Reference
LC_{LO} (3 h)		10 000 ppm	ITII 1981
LC_{LO} (inhalation)(aqueous)		5000 ppm	RTECS 1979
LD_{LO} (anhydrous)		132 mg/kg	RTECS (on-line) 1981
LD_{LO} (oral)(aqueous, 44% NH_3)		43 mg/kg	RTECS 1979
TC_{LO} (irritation only)		20 ppm	RTECS (on-line) 1981
TC_{LO} (eye)(aqueous)		700 ppm	RTECS 1979
TC_{LO} (inhalation - irritation (44% aqueous)		408 ppm	RTECS 1979
TC_{LO} (skin)		1000 mg/kg Suspect carcinogen	ITII 1981

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is one measure of the potential of a substance to cause injury via inhalation. It is calculated as follows:

ITI = 1315.12 (vapour pressure, in mm Hg/TLV® in ppm)
Vapour pressure @ 21°C = 888 kPa = 6661 mm Hg
TLV® = 25 ppm
ITI = 3.5×10^5 @ 21°C

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
2% to 3%	TC_{LO}. Burns wet skin	AAR 1981
21 000 mg/m^3	Skin burns. Vesiculation	NIOSH/OSHA 1981
7000 mg/m^3	Irritating to moist skin	NIOSH/OSHA 1981
>1400 mg/m^3 (few seconds)	Skin burns, blisters	NSC 1979
700 mg/kg/m^3	TC_{LO}. Suspected carcinogen	ITII 1981
1:1 aqueous solution (13 min)	Intra-epidermal blister	Patty 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
698 ppm	TC_{LO}. Irritation	AAR 1981
One incident	Corneal staining, gross chemoisis, loss of pupillary reaction, lens pigmentation, uveitis	Patty 1981
134 ppm (5 min)	Lacrimation, eye irritation	NIOSH 1974
20 ppm, average (occupational)	Some workers dislayed conjunctivitis, "unaccustomed" workers complained of eye irritation	NIOSH 1974
SPECIES: Rabbit		
750 µg	Severe irritation (aqueous)	RTECS 1979
44 µg	Moderate irritation (aqueous)	RTECS 1979

7.3 Threshold Perception Properties

7.3.1 Odour (in air unless otherwise specified).

Odour Characteristics:	Extremely pungent
Odour Index:	167 300 (AAR 1981)

Parameter	Media	Concentration	Reference
Odour Threshold		53 ppm	APM 1967
		50 ppm	Doc. TLV 1980
		46.8 ppm	Leonardos 1969
		<5 ppm	APM 1967
		1 ppm	Doc. TLV 1980
		1 to 5 ppm	NIOSH/OSHA 1981
		0.6 to 0.7 ppm	Saifutdinov 1966. <u>IN</u> NIOSH 1974
Recognition Threshold		46.8 ppm	Sullivan 1969
		0.7 ppm	Sullivan 1969
		0.037 ppm	Sullivan 1969

Parameter	Media	Concentration	Reference
Upper Recognition Threshold		52.3 ppm	AAR 1981
Upper Odour Threshold		2.6 ppm	OHM-TADS 1977
Median Odour Threshold		0.5 ppm	OHM-TADS 1977
Low Odour Threshold		0.32 ppm	OHM-TADS 1977
Threshold Odour Concentration		0.026 to 37 mg/m^3	Verschueren 1977
Threshold Odour Concentrations		0.037 to 0.049 ppm	AAR 1981
Individual Perception Threshold		6.6 x 10^{-4} ppm	AAR 1981
Individual Perception Threshold		0.00066 to 0.049 ppm	Verschueren 1977
Population Identification Threshold		21.4 to 46.8 ppm	AAR 1981
100% Recognition Concentration		55 ppm	Verschueren 1977

7.3.2 **Taste.** Taste Characteristic: Bitter.

Parameter	Media	Concentration	Reference
Median Taste Threshold	Water	34 ppm	ASTM 1980
Median Taste Threshold	Coffee	34 ppm	OHM-TADS 1977
Lower Taste Threshold	-	0.037 ppm	AAR 1981

7.4 Effect Studies

SUMMARY OF HUMAN EXPOSURE (Kirk-Othmer 1978)

Concentration (ppm)	Effects
20	first perceptible odour
40	a few individuals may suffer slight eye irritation
100	noticeable irritation of eyes and nasal passages, and of upper respiratory tract
400	severe irritation of the throat, nasal passages, and upper respiratory tract

Concentration (ppm)	Effects
700	severe eye irritation; no permanent effect if the exposure is limited to less than 1/2 h
1700	serious coughing, bronchial spasms; less than 1/2 h of exposure may be fatal
5000	serious edema, strangulation, asphyxia; fatal almost immediately

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
21 000 mg/m^3 (5 min)	LC_{LO}	RTECS 1979
7000 mg/m^3 (3 h)	LC_{LO}	ITII 1981
7000 mg/m^3	Immediate coughing, dyspnea, vomiting, death due to heart failure 6 hours after exposure	Mulder et al. 1967. IN NIOSH 1974
7000 to 3500 mg/m^3	Respiratory spasm and rapid asphyxia	Braker 1977
7000 to 3500 mg/m^3 (0.5 h)	Rapidly fatal for short exposure	Ammonia 1979
4550 to 1750 mg/m^3	Dyspnea, bronchospasm, pulmonary edema	NIOSH/OSHA 1981
4550 to 1750 mg/m^3 (0.5 h)	Dangerous for even short exposure	Ammonia 1979
2100 to 1400 mg/m^3	Convulsive coughing, severe eye irritation	Braker 1977
1204 mg/m^3	TC_{LO}. Pulmonary effects	AAR 1981
1190 mg/m^3	Lung edema	NSC 1979
490 mg/m^3 (prolonged)	May scar cornea	NSC 1979
490 to 280 mg/m^3	Immediate eye, nose, throat irritation	Patty 1981
350 mg/m^3 (0.5 h)	Upper respiratory irritation, lacrimation	Patty 1981

Exposure Level (and Duration)	Effects	Reference
350 mg/m^3 (0.5 h)	Irregular minute ventilation hypernea, increased blood pressure, pulse rate, lacrimation, upper respiratory irritation	Silverman et al. IN NIOSH 1974
350 mg/m^3 (0.5 to 1 h)	Death	Ammonia 1979
350 to 210 mg/m^3 (1 h)	Maximum tolerable level	Patty 1981
350 to 210 mg/m^3 (0.5 to 1 h)	Maximum concentration allowable for short exposure	Ammonia 1979
288 mg/m^3	TC_{LO}. Throat irritation (aqueous solution)	RTECS 1979
140 mg/m^3 (2 h)	Severe irritation. No effect on ventilatory capacity, forced expiratory and inspiratory volumes	Patty 1981
94 mg/m^3 (5 min)	Eye irritation, lacrimation, discomfort of nose, throat, chest	Ind. Biotest Labs 1973. IN NIOSH 1974
70 mg/m^3 (8 h)	Maximum no-effect level	Braker 1977
70 mg/m^3 (2 to 6 h)	Nasal irritation (6 of 6), eye irritation (3 of 6), throat irritation (2 of 6)	Patty 1981
70 to 35 mg/m^3 (1 h)	Maximum concentration allowable for short exposure	Ammonia 1979
50 mg/m^3 (5 min)	Nasal, throat, eye irritation	Ind. Biotest Labs 1973. IN NIOSH 1974
35 mg/m^3 (2 to 6 h)	Mild nasal irritation	NIOSH/OSHA 1981
35 mg/m^3 (10 min)	Moderate irritation (4 of 6), odour highly penetrating	MacEwan et al. 1970. IN NIOSH 1974
35 to 22 mg/m^3 (5 min)	Dryness of nose	Ind. Biotest Labs 1973. IN NIOSH 1974
22 mg/m^3 (5 min)	Nasal dryness (1 of 10)	NIOSH/OSHA 1981
21 mg/m^3 (10 min)	Some irritation, odour highly penetrating (2 of 6)	MacEwan et al. 1970. IN NIOSH 1974

Exposure Level (and Duration)	Effects	Reference
17 mg/m^3 (2 to 6 h)	Nasal irritation (2 of 6)	Patty 1981
14 mg/m^3	TC_{LO} (irritant)	RTECS 1979
SPECIES: Guinea Pig		
17 500 to 14 000 mg/m^3 (5 min)	Respiratory irritation, permanent blindness (1 of 2)	Underwriter's Lab 1933. IN NIOSH 1974
17 500 to 14 000 mg/m^3 (9 min)	Death (1 of 2)	Underwriter's Lab 1933. IN NIOSH 1974
17 500 to 14 000 mg/m^3 (30 min)	Marked respiratory difficulties, blindness (1 of 1)	Underwriter's Lab 1933. IN NIOSH 1974
4200 to 3500 mg/m^3 (30 s)	Lacrimation, nasal discharge, laboured breathing	Underwriter's Lab 1933. IN NIOSH 1974
4200 to 3500 mg/m^3 (5 min)	Inflamed eyes, nose, irregular respiration, retching, temporary blindness	Underwriter's Lab 1933. IN NIOSH 1974
4200 to 3500 mg/m^3 (30 min)	Violent coughing, permanent blindness (1 of 2)	Underwriter's Lab 1933. IN NIOSH 1974
4200 to 3500 mg/m^3 (60 min)	Shallow breathing, permanent blindness	Underwriter's Lab. 1933. IN NIOSH 1974
4200 to 3500 mg/m^3 (120 min)	Barely perceptible breathing, blindness	Underwriter's Lab. 1933. IN NIOSH 1974
3500 mg/m^3 (5 min)	LC_{LO}	RTECS 1979
SPECIES: Rabbit		
7250 mg/m^3 (1 h)	LC_{50} approximate. Upper respiratory tract protects trachea and bronchi from NH_3 injury	Boyd et al. 1944. IN NIOSH 1974
7050 mg/m^3 (1 h)	LD_{50}	Patty 1981
4900 mg/m^3 (1 h)	LC_{LO}	RTECS 1979
1540 mg/m^3 (45 min)	Mean decrement in ciliary activity of 17%. Nasopharynx absorption of NH_3, 95%	Dalhamn 1963. IN NIOSH 1974

Exposure Level (and Duration)	Effects	Reference
754 mg/m^3 (1 h)	LC_{50}	Sax 1979
700 to 350 mg/m^3 (5 min)	Arrest of ciliary activity of incised trachea	Dalhamn and Sjoholm 1963. IN NIOSH 1974
700 to 322 mg/m^3 (5 min)	Ciliary activity stopped in resected trachea	Dalhamn 1963. IN NIOSH 1974
350 mg/m^3 (5 min)	Arrest of ciliary activity in resected sections of trachea	Cralley 1942. IN NIOSH 1974
280 mg/m^3 (10 min)	Arrest of ciliary activity in resected sections of trachea	Cralley 1942. IN NIOSH 1974
280 to 189 mg/m^3 (5 min)	Ciliary beat ceased or greatly reduced	Dalhamn and Sjoholm 1963. IN NIOSH 1974
140 mg/m^3 (9.5 min)	Temporary arrest of ciliary activity	Cralley 1942. IN NIOSH 1974
70 mg/m^3 (2.5 to 3 h)	Decrease by 1/3 in respiration rate. Respiratory depth increased with exposure time. Blood CO_2 increased	Mayan and Merilan 1972. IN NIOSH 1974
35 mg/m^3 (2.5 to 3 h)	Decrease by 1/3 in respiration rate	Mayan and Merilan 1972. IN NIOSH 1974
SPECIES: Cat		
7250 mg/m^3 (1 h)	LC_{50} approximate. Upper respiratory tract absorbs ammonia, protecting trachea and bronchi from NH_3 injury, and extending survival abilities	Boyd et al. 1944. IN NIOSH 1974
7050 mg/m^3 (1 h)	LD_{50}	Patty 1981
4900 mg/m^3 (1 h)	LC_{LO}	RTECS 1979
754 mg/m^3 (1 h)	LC_{50}	Sax 1979
700 mg/m^3 (10 min)	TC_{LO}	RTECS (on-line) 1981
SPECIES: Rat		
7600 mg/m^3 (2 h)	LC_{50}	Patty 1981
5100 mg/m^3 (1 h)	LC_{50}	OHM-TADS 1981

Exposure Level (and Duration)	Effects	Reference
3500 mg/m^3 (30 to 40 min)	Death. From 0 to 3500 mg/m^3, gradient increased oxygen consumption (to 150%)	Ammonia 1979
2100 mg/m^3 (2.5 to 3 h)	Death	Ammonia 1979
1400 mg/m^3 (4 h)	LC_{LO}	ITII 1981
700 mg/m^3 (16 h)	Death	Ammonia 1979
700 mg/m^3 (16 h)	No noticeable effects during exposure. One rat died 12 hours later - showed congestion of brain, liver, kidneys, hemorrhages in lungs, pulmonary edema	Weedon et al. 1940. IN NIOSH 1974
63 mg/m^3 (5 s) 32 mg/m^3 (10 s) 14 mg/m^3 (20 s) 5 mg/m^3 (150 s) 2 mg/m^3 (7 to 8 min)	Ciliary activity of incised tracheas ceased temporarily	Dalhamn 1956. IN NIOSH 1974
SPECIES: Mouse		
10 500 to 1750 mg/m^3	In combination with CO, CO_2, prolonged survival before collapse. Mechanism not known	Ammonia 1979
9060 to 6140 mg/m^3 (10 min)	Great excitement, severe eye and upper respiratory tract irritation. Death of 100 (n = 180) animals during exposure, 7 animals between days 6 and 10 after exposure	Silver and McGrath 1948. IN NIOSH 1974
7105 mg/m^3 (10 min)	LC_{50}	Silver and McGrath 1948. IN NIOSH 1974
3500 mg/m^3 (10 to 20 min)	Death	Ammonia 1979
3386 mg/m^3 (1 h)	LC_{50}	RTECS 1981
3360 mg/m^3 (1 h)	LC_{50}	OHM-TADS 1981
3310 mg/m^3 (2 h)	LC_{50}	Patty 1981
2100 mg/m^3 (2.5 to 3 h)	Death. From 0 to 2,100 mg/m^3, gradient increased oxygen consumption (to 127%)	Ammonia 1979

Exposure Level (and Duration)	Effects	Reference
700 mg/m^3 (16 h)	No noticeable effects during exposure. One animal died 12 hours after exposure - showed congestion of brain, liver, kidneys, hemorrhages in lungs, pulmonary edema	Weedon et al. 1940. IN NIOSH 1974
700 mg/m^3 (16 h)	Death	Ammonia 1979
210 mg/m^3 (10 min)	Decrease in respiratory rate by 15%	Kane 1979
Chronic Exposures		
SPECIES: Human		
88 mg/m^3 (occupational exposures)	Definitely irritating	Pagnotto (personal communication). IN NIOSH 1974
88 to 70 mg/m^3 (daily)	Upper respiratory and eye irritation	Pagnotto (personal communication). IN NIOSH 1974
32 mg/m^3 (occupational exposure)	Some eye irritation, strong odour	Pagnotto (personal communication). IN NIOSH 1974
26 to 6 mg/m^3 (occupational exposures)	Odour fatigue	Pagnotto (personal communication). IN NIOSH 1974
20 to 10 mg/m^3 (occupational exposures)	Very slight eye irritation	Pagnotto (personal communication). IN NIOSH 1974
20 to 3 mg/m^3	Hardly noticeable to moderate eye irritation	NIOSH/OSHA 1981
20 to 2 mg/m^3 (occupational exposures)	Odour marked but not disagreeable	Pagnotto (personal communication). IN NIOSH 1974
18 to 14 mg/m^3 (occupational exposure)	Maximum concentration occupationally acceptable without complaint	Doc. TLV 1980
14 mg/m^3 (occupational exposures)	Conjunctivitis, eye and respiratory irritation in unacclimatized workers	Pagnotto (personal communication). IN NIOSH 1974

Exposure Level (and Duration)	Effects	Reference
SPECIES: Monkey		
470 mg/m^3 (90 d)	Interstitial inflammatory processes in lungs	Coon et al. 1970. IN NIOSH 1974
155 mg/m^3 (8 h/d, 5 d/wk for 6 wk)	Focal pneumonitis, 1 animal of 3	Coon et al. 1970. IN NIOSH 1974
40 mg/m^3 (114 d - continuous)	No signs of toxicity. No lung abnormalities	Coon et al. 1970. IN NIOSH 1974
SPECIES: Pig		
102 mg/m^3 (5 wk)	Excessive nasal, lacrymal, and oral secretions. Coughing	Stombaugh et al. 1969. IN NIOSH 1974
74 mg/m^3 (6 wk) (36 to 112 mg/m^3)	Weanling pigs experienced slight eye irritation, lacrimation, photophobia, but acclimatization occurred	Doig and Willoughby 1971. IN NIOSH 1974
43 mg/m^3 (5 wk)	Excessive nasal, lacrymal, and oral secretions. Coughing, although three times less frequent than observed at 102 mg/m^3	Stombaugh et al. 1969. IN NIOSH 1974
SPECIES: Dog		
770 mg/m^3 (8 h/d, 5 d/wk for 6 wk)	Mild to moderate eye irritation, laboured breathing, followed by adaptation	Coon et al. 1970. IN NIOSH 1974
470 mg/m^3 (90 d)	Eye irritation, heavy lacrimation and nasal discharge. Interstitial inflammatory processes in lungs	Coon et al. 1970. IN NIOSH 1974
40 mg/m^3 (114 d - continuous)	No signs of toxicity, no lung abnormalities	Coon et al. 1970. IN NIOSH 1974
SPECIES: Rabbit		
10 500 to 3500 mg/m^3 (continuous)	Lived for 53 days, compared with 4 to 15 days survival of guinea pigs	Ammonia 1979
770 mg/m^3 (30 d, 8 h/d)	Mild to moderate eye irritation, laboured breathing, followed by adaptation	Coon et al. 1970. IN NIOSH 1974

Exposure Level (and Duration)	Effects	Reference
470 mg/m^3 (90 d)	Erythema, corneal opacity. Interstitial inflammatory processes in lungs	Coon et al. 1970. IN NIOSH 1974
40 mg/m^3 (114 d)	No signs of toxicity, no lung abnormality	Coon et al. 1970. IN NIOSH 1974
SPECIES: Guinea Pig		
770 mg/m^3 (30 d, 8 h/d)	No specific inflammatory changes in lungs	Coon et al. 1970. IN NIOSH 1974
470 mg/m^3 (90 d)	Death (4 of 15), interstitial inflammatory processes in lungs	Coon et al. 1970. IN NIOSH 1974
119 mg/m^3 (60 d, 6 h/d)	No adverse effects	Weatherby 1952. IN NIOSH 1974
119 mg/m^3 (90 d, 6 h/d)	Congestion of spleen, liver, kidney, degeneration in suprarenal gland, increased blood destruction. Lungs normal	Weatherby 1952. IN NIOSH 1974
102 to 43 mg/m^3 (5 wk)	Respiratory irritation increased with concentration, food intake and weight gain decreased with concentration	Ammonia 1979
40 mg/m^3 (114 d - continuous)	No signs of toxicity, no lung abnormalities	Coon et al. 1970. IN NIOSH 1974
SPECIES: Rat		
770 mg/m^3 (30 d, 8 h/d)	Nonspecific inflammatory changes in lungs	Coon et al. 1970. IN NIOSH 1974
770 mg/m^3 (90 d)	Death (13 of 15). Interstitial inflammatory processes in lungs	Coon et al. 1970. IN NIOSH 1974
455 mg/m^3 (65 d)	Mild dyspnea, nasal irritation, 50 of 51 died by day 65	Coon et al. 1970. IN NIOSH 1974
262 mg/m^3 (90 d)	Mild nasal irritation (25%), slightly elevated leukocyte count (10%)	Coon et al. 1970. IN NIOSH 1974
127 mg/m^3 (90 d)	No abnormalities	Coon et al. 1970. IN NIOSH 1974

Exposure Level (and Duration)	Effects	Reference
63 to 20 mg/m^3 (50 d)	No effect on weight, hematology at 22°C. Slight weight loss at 10°C	Patty 1981
4 mg/m^3 (114 d)	No signs of toxicity	Patty 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
43 mg/kg	LD_{LO} (aqueous NH_3)	RTECS 1979
SPECIES: Rat		
350 mg/kg	LD_{50} (anhydrous and aqueous)	RTECS 1979
SPECIES: Cat		
750 mg/kg	LD_{LO} (aqueous NH_3)	RTECS 1979

7.4.3 Mutation Data.

Exposure Level (and Duration)	Effects	Reference
SPECIES: *E. coli*		
1500 ppm (3 h)	Heritable genetic alterations	RTECS 1979
SPECIES: Rat		
19.8 mg/m^3 (16 wk)	Chromosomal aberrations in cells	RTECS 1979

7.5 Symptoms of Exposure

Human contact with ammonia may be in the form of gas (from anhydrous source or aqueous solution), anhydrous liquid or aqueous solution. The effects of gaseous ammonia, in general, can range from mild irritation to severe corrosion of sensitive membranes of the eyes, nose, throat and lungs. Inhalation is considered to be the primary route for human exposure to ammonia. The most dangerous consequence of exposure to the gas is considered to be pulmonary edema. Also, the gas is particularly irritating to moist skin surfaces. Anhydrous liquid ammonia can cause severe injury by freezing tissue (first and second degree burns on contact) and subjecting it to caustic action. The reports of injury due to ingestion of ammonia (aqueous) are few and are primarily from medical records of suicide attempts or accidental ingestion by children. Aqueous ammonia differs from other alkalis in that it is volatile, evolving ammonia gas. Due to its corrosiveness, the effects of swallowing as little as 10^{-4} m^3 can result in the perforation of the esophagus, gastric strictures, necrosis and even death. The burns and lesions caused by ammonia (aqueous) are the result of the saponification of the lipids of the epithelial tissue and solvent action of proteins. The injuries often require partial or complete replacement of the affected organ with intestinal tissue. Due to its volatility, the organs affected by the ingestion of aqueous ammonia are not restricted to the mouth, esophagus and stomach. It can cause pneumonitis in the lungs and irritation of the eye tissue. These latter reactions, however, are usually less severe and the patients respond to conventional supportive treatment. In general, the inhalation or ingestion of ammonia does not produce signs of systemic intoxication; evidence indicates no significant accumulative effects of chronic exposure. The ammonia removal mechanisms of the body are very rapid and efficient. Ammonia has not been shown to be carcinogenic, teratogenic or mutagenic in man or other animals.

It has been shown in studies using sheep that unionized ammonia (NH_3), as opposed to ionized ammonia (NH_4^+), is the toxic form. It was demonstrated that the rate of ammonia production from the enzymatic hydrolysis of urea by bacteria in the rumen of sheep was greater than the rate at which the bacteria were using the ammonia for protein synthesis. The excess ingestion of urea, which is used as a nonprotein source of nitrogen in ruminant nutrition, can result in toxic effects ranging from restlessness to death. The absorption of the unionized ammonia into the blood was demonstrated to be related to the pH of the ruminal fluid. At pH values of 6.21 and 6.45, no ammonia was absorbed; however, increasing the pH to 7.55, 7.58 and 7.65 resulted in increased ammonia absorption across the rumen epithelial lining. Other studies show that the passage of ammonia across the blood-brain barrier is directly related to the effect of a given ammonium compound on the blood pH. It appears cell membranes are relatively impermeable to ionized ammonia (NH_4^+) and permeable to unionized ammonia (NH_3).

General symptoms of exposure to ammonia are listed below, and in most cases, have not been specifically referenced. Only those symptoms of an unusual nature have their sources indicated. The references used for the above presentation are Kirk-Othmer (1978), Gosselin (1976) and API (1981).

7.5.1 Inhalation.

1. Irritation of nose, throat, eyes (burning sensation).
2. Lacrimation, runny nose.
3. Sneezing, coughing.
4. Redness of the mucous membranes of the lips, mouth, nose and pharynx (Dreisbach 1980).
5. Hoarseness, tightness of throat (Morris 1956. IN NIOSH 1974).
6. Difficulty in breathing, swallowing, due in part to reflex laryngeal spasm (MCA 1947).
7. Laryngitis, tracheitis (Slot 1938. IN NIOSH 1974).
8. Tightness in the chest (Dreisbach 1980).
9. Fits of coughing. Persistent and residual cough.
10. Higher concentrations cause swelling of the lips, eyelids, and conjunctiva.
11. Vesiculation (Proctor 1978).
12. Moist rales in lungs (Caplin 1941. IN NIOSH 1974).
13. Pink frothy sputum (Proctor 1978).
14. Decreased vital capacity, diffusion capacity, and increased residual volume/total lung capacity (Lepine and Soncy 1962. IN NIOSH 1974).
15. Increased blood pressure, blood ammonia, and serum nonprotein nitrogen (Schmidt and Vallencourt 1948. IN NIOSH 1974).
16. Vomiting (Sax 1979).
17. Temporary blindness (Dreisbach 1980).
18. Dyspnea with cyanosis (Walten 1972. IN NIOSH 1974).
19. Bronchiectasis, pulmonary obstruction, leading to hypoxemia (Kass et al. 1972. IN NIOSH 1974).
20. Chemical pneumonia or bronchitis.
21. Loss of bronchial epithelium (Walten 1972. IN NIOSH 1974).
22. Epidermal carcinoma of nasal septum (Shimkin et al. 1954. IN NIOSH 1974).

23. Congested kidneys, early hemorrhagic nephritis (Slot 1938. IN NIOSH 1974).
24. Pulmonary edema.
25. Sudden death (Lefèvre 1980).

7.5.2 Ingestion.

1. Irritation of mouth, throat.
2. Pain in mouth, throat, chest, upper abdomen.
3. Nausea, vomiting.
4. Cold, clammy skin.
5. Rapid, weak pulse.
6. Gastric or esophageal perforation may occur later, with greater abdominal pain and fever.
7. Lung irritation and pulmonary edema may appear after 12 to 24 hours delay (Dreisbach 1980).
8. Convulsions.
9. Collapse.
10. Coma, perhaps preceeded by a period of convulsions.
11. Death.

7.5.3 Skin Contact.

1. Irritation, reddening, local edema.
2. Dermatitis.
3. Chemical burns, blisters which rupture and bleed (Patty 1981).
4. Contact with liquid ammonia will produce frostbite, as well as corrosion damage.

7.5.4 Eye Contact.

1. Conjunctival irritation.
2. Swollen eyelids, spasms of the ocular muscles (NIOSH/OSHA 1981).
3. Ulceration of conjunctiva, cornea.
4. Corneal edema, causing opacities, uveitis, impaired acuity (Dupuy et al. 1968. IN NIOSH 1974).
5. Constricted pupils (White 1971. IN NIOSH 1974).
6. Loss of pupillary reactions (Patty 1981).
7. Cataract changes (Kass et al. 1972. IN NIOSH 1974).
8. Temporary blindness (MCA 1960).

7.6 Human Toxicity to Decay or Combustion Products

Although ammonia is not considered to be a serious fire or explosion hazard, a large and intense energy source may promote ignition or an explosion under the right conditions. Normal combustion products are nitrogen and water. The ignition temperature of ammonia in air is 650°C. Ammonia begins to dissociate to nitrogen and hydrogen at about 450-500°C (Kirk-Othmer 1978).

7.6.1 Hydrogen and Nitrogen. Hydrogen is a colourless, tasteless, odourless gas which, when mixed with air, forms explosive mixtures. With an ignition source, the air-gas mixture burns with a very hot, nonluminous flame (i.e., difficult to see). Nitrogen is nontoxic and acts as a simple asphyxiant.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Ammonia with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Heat		X					X						Difficult to ignite; requires high concentration in air before it catches fire	Sax 1979
Fire			X										Moderate explosion hazard when gaseous ammonia is exposed to flame	Sax 1979
SPECIFIC CHEMICALS														
Acetaldehyde											X		With anhydrous	NFPA 1978
Acrolein					X						X			NFPA 1978
Boron				X									Evolves hydrogen	NFPA 1978
Boron Triiodide	X													NFPA 1978
Bromine			X										Forms explosive nitrogen tribromide	NFPA 1978
Bromine Pentafluoride	X		X											NFPA 1978

8.1 Compatibility of Ammonia with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Calcium	X	X											Reacts at ambient, incandesces at higher temperatures	Bretherick 1979
Chloric Acid			X											NFPA 1978
Chlorine			X										With heat forms explosive nitrogen trichloride	NFPA 1978
Chlorine Azide			X										Forms an explosive liquid	Bretherick 1979
Chlorine Monoxide			X										Upon mixing	NFPA 1978
Chlorine Trifluoride			X										Upon mixing	NFPA 1978
1-Chloro-2,4-Dinitrobenzene	X		X										In a closed container	Bretherick 1979
Chloroformamidinium Nitrate											X			Bretherick 1979
o- or p-Chloro-Nitrobenzene	X								X				In a closed container	Bretherick 1979
Chlorosilane				X									May form flammable trisilylammonia	NFPA 1978
Chromic Anhydride		X				X							Decomposes with incandescence	NFPA 1978

8.1 Compatibility of Ammonia with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Chromyl Choride		X											Causes ignition	NFPA 1978
Ethylene Dichloride			X										Upon mixing	NFPA 1978
Ethylene Oxide			X										Under high pressure in a closed vessel	NFPA 1978
Fluorine		X											Upon mixing or contact	NFPA 1978
Gold			X										Produces fulminate-like compounds that explode when dried	NFPA 1978
Gold (III) Chloride			X										Gives explosive fulminating compound	Bretherick 1979
Hydrogen Bromide											X		Upon contact	NFPA 1978
Hypochlorous Acid			X				X						Gaseous ammonia and hypochlorous acid explode on contact, producing chlorine	NFPA 1978
Iodine			X										Spontaneously	NFPA 1978
Magnesium Perchlorate	X		X								X		On contact with gas	NFPA 1978

8.1 Compatibility of Ammonia with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Mercury			X										Produces explosive compounds	NFPA 1978
Nitric Acid		X											Burns in an atmosphere of nitric acid vapour	NFPA 1978
Nitrogen Tetroxide			X										Reacts explosively even when cold	NFPA 1978
Nitrogen Trichloride			X			X					X		Explosive, decomposition on contact	Bretherick 1979
Nitrogen Trifluoride			X										Explosive upon ignition	NFPA 1978
Nitryl Chloride											X		Liquid ammonia reacts violently at all temperatures	NFPA 1978
Oxygen (liquified)			X											Bretherick 1979
Oxygen Difluoride						X							Reacts to produce white fumes	NFPA 1978
Picric Acid			X										Forms explosive salts	NFPA 1978

8.1 Compatibility of Ammonia with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Phosphorus Pentoxide												X	Reacts vigorously	NFPA 1978
Phosphorus Trioxide											X		Reacts violently if warm	NFPA 1978
Potassium			X										May form explosive nitrogen trioxide	Bretherick 1979
Potassium Chlorate											X		With gaseous ammonia	NFPA 1978
Potassium Ferricyanide			X										May explode on mixing	NFPA 1978
Silver			X										Produces explosive fulminate-like compounds	NFPA 1978
Silver Chloride			X										Produces explosive silver nitride	Bretherick 1979
Silver Nitrate			X										May explode after prolonged contact	Bretherick 1979
Stibine			X										Heated mixture explodes	Bretherick 1979
Sulphur			X										May form explosive sulphur nitride under certain conditions	NFPA 1978

8.1 Compatibility of Ammonia with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Sulphur Dichloride			X										Forms explosive sulphur nitride	NFPA 1978
Tellurium Halides			X										Forms an explosive mixture on heating	Bretherick 1979
Tetramethylammonium Amide			X										Decomposes explosively on contact	Bretherick 1979
Thiocarbonyl Azide Thiocyanate			X										Reacts explosively	Bretherick 1979
Thionyl Chloride			X										May form explosive nitrogen trichloride	Bretherick 1979
Thiotrithiazyl Chloride			X										Rapidly absorbs ammonia and then explodes	Bretherick 1979
Trichloromelamine		X	X										Contamination by ammonia can cause reaction with flame and with explosion depending on conditions	NFPA 1978
CHEMICAL GROUPS														
Esters	X												Hydrolysis to the associated salt and alcohol	EPA 600/ 2-80-076

8.1 Compatibility of Ammonia with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Alkali and Alkaline Earth Metals	X			X									Yields hydrogen	EPA 600/ 2-80-076
Chlorites			X										Reacts to produce explosive ammonium chloride	NFPA 1978
Epoxides	X				X									EPA 600/ 2-80-076
Explosives	X		X										Reaction can generate enough heat to detonate explosive	EPA 600/ 2-80-076
Halogenated Compounds			X										Reacts with main hologens or halogenated compounds	Bretherick 1979
Halogenated Organics - Aliphatic	X			X									Yields flammable olefins and acetylene	EPA 600/ 2-80-076
Isocyanates	X				X	X							Monoisocyanates decompose. Diisocyanates polymerize	EPA 600/ 2-80-076
Ketones	X										X		Self-condensation of the ketone	EPA 600/ 2-80-076

8.1 Compatibility of Ammonia with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Nitroalkanes and Nitroaromatics			X										Forms salts that are explosive when dry	EPA 600/ 2-80-076
Non-Oxidizing Mineral Acids	X								X		X			EPA 600/ 2-80-076
Organic Acids	X								X					EPA 600/ 2-80-076
Organophosphates	X													EPA 600/ 2-80-076
Oxidizing Agents	X		X										Reacts generally with oxidizing agents	Bretherick 1979
Oxidizing Mineral Acids	X								X		X			EPA 600/ 2-80-076
Polymerizable Compounds	X				X									EPA 600/ 2-80-076
Water Reactive Substances	X		X	X			X				X		May also result in unstable mixtures	EPA 600/ 2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original sources has been essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is also recognized that countermeasures vary from situation to situation, and thus what may be inappropriate for one situation may be correct in another. These procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Ammonia is generally not considered to be a serious fire or explosion hazard; however, a large and intense energy source may cause ignition and/or an explosion. The flammability/explosion concentration range is generally given as 16 to 25 percent by volume in air at atmospheric pressure. Some references give values of 15 to 28 percent (EST 1978); others give values of 16 to 27 percent at 0°C and 15.5 to 28 percent at 100°C (Ullmann 1974). Ignition tests carried out with liquid ammonia in an open pan resulted in brief flames but no sustained fire. When ignited, however, ammonia flames are nonluminous, with low radiation fluxes. Detonations of ammonia-air mixtures are apparently limited to cases where the mixture is confined. Very low concentrations, 1 percent or less, of ammonia in water will evolve vapours in the flammability range. The presence of oil or other combustible materials increases the fire hazard. Dissociation to hydrogen and nitrogen begins above 450°C. Containers of ammonia may rupture with explosive violence if subjected to the heat of a fire (Kirk-Othmer 1978; CE 1978; NSC 1979; GE 1979; ERG 1980).

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to help prevent rupture and to protect men effecting the shut-off (GE 1979; NFPA 1978).

Small fires: Dry chemical or CO_2.
Large fires: Water spray, fog or foam.

Move containers from fire area if this can be done without risk. Stay away from tank ends (ERG 1980).

9.1.3 Evacuation. The following information consists of evacuation distances which appear in the literature. Important parameters such as spill quantity, concentration level to which evacuation is suggested, and environmental conditions, may not be defined. Readers are advised to evaluate the use of these values with those derived from the methods to calculate hazard zones in Section 5.3.

The following are recommended evacuation distances from the immediate danger area of a spill based on prevailing winds of 10 to 19 km/h (EAG 1978).

Approximate Size of Spill	Distance to Evacuate From Immediate Danger Area	For Maximum Safety Downwind Evacuation Should Be
20 m^2	35 m (48 paces)	320 m long, 160 m wide
35 m^2	55 m (72 paces)	480 m long, 320 m wide
55 m^2	75 m (96 paces)	645 m long, 320 m wide
75 m^2	80 m (108 paces)	645 m long, 480 m wide

In the event of an explosion, the minimum safe distance from flying fragments is 600 m in all directions.

9.1.4 Spill Actions.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition (GE 1979). Use water spray to reduce vapours and to protect men effecting the shut-off (ERG 1980; GE 1979; NFPA 1978). Avoid skin contact or inhalation (GE 1979). If a leaking container cannot be stopped by tightening the packing nut, the container should be removed to the outdoors or to an isolated, well-ventilated area (HCG 1981; MCA 1960).

If a leak in a container cannot be controlled, the container should be turned into a position where the leak is uppermost and only gaseous and not liquid ammonia is released. Any escaping gas can be absorbed by water spray (NSC 1979). If necessary, liquid ammonia can be discharged into a vessel containing sufficient water (10 parts of water to 1 part of ammonia) to absorb it (HCG 1981).

If the ammonia in a container is colder than the available water supply, which may be the case in a leak situation, water must not be sprayed on the container walls since it will heat the ammonia and aggravate any gas leak (HCG 1981).

If aqueous ammonia leaks from a container through a rupture or a hole, it can be plugged by using the following recommended materials: polyester (glad bag) and Imid polyester (brown-in-bag) (EPA 600/2-76-300). Cellosize WP3H (hydroxyethyl cellulose), as an absorbent material, has shown possible applicability for vapour suppression and containment of aqueous ammonia solutions (Braley 1982).

9.1.4.2 Spills on land. Contain if possible any spilled liquid (liquefied ammonia or ammonia-contaminated water) by dyking or use of lagoons. Neutralize with dilute acid if this can be done without risk (EPA 670/2-75-042). If neutralization is not possible, every effort should be made to recover the liquid by an appropriate technique.

9.1.4.3 Spills in water. Contain if possible by using dams or water diversion techniques. Contained water may be treated as described below.

9.1.5 Cleanup and Treatment.

9.1.5.1 Spills in water (spills of ammonia/water mixture or ammonium hydroxide in water). Sodium dihydrogen phosphate is recommended as an in situ neutralizing agent to avoid overdosing resulting in too great a pH decrease (CG-D-16-77). Clinoptilolite and other natural zeolites are ammonium-selective and should also be considered (OHM-TADS 1981).

9.1.5.2 General. For treatment of contaminated water, the following alternative procedures are recommended (EPA 600/2-77-227). First: dilution with water followed by neutralization with hydrochloric acid (pH 7.0). Second: gravity separation of the solids followed by neutralization with sulphuric acid (pH 6.0 to 7.0), and dual media filtration. Return backwashing of the filtration system to gravity separation. Finally: treatment of filtered water through an ion exchange resin followed by neutralization with sodium hydroxide (pH 7.0) is also recommended.

The following treatment processes have shown possible applicability for spill countermeasures:

Process	% Removal
Air stripping	90 (max) (EPA 600/8-80-042E)
Chemical Oxidation	36 (EPA 600/2-76-109)
Reverse Osmosis	88 to 98 (EPA 600/2-76-109)

9.1.6 Disposal. Waste aqueous ammonia or ammonia-contaminated water must never be discharged directly into sewers or surface waters. The basic solution must be neutralized at the spill site or at a waste management facility. The resulting solution must be further treated to comply with existing federal and provincial regulations before the "clean" water can be released to the environment. Any resulting sludge can be disposed of to a secure landfill; any contaminated soil or sediment (after further treatment) can be returned to the environment if all regulations are adhered to.

9.1.7 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be ammonia (in the anhydrous or aqueous form):

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate clothing necessary to prevent any possibility of repeated or prolonged skin contact with liquid anhydrous ammonia or aqueous solutions of ammonia. The above personal protection should also be worn to prevent the skin from freezing upon contact with vessels containing liquid anhydrous ammonia (NIOSH/OSHA 1981).
- Splash-proof safety goggles can also be worn where there is any possibility of liquid anhydrous ammonia or aqueous solutions of ammonia contacting the eyes (NIOSH/OSHA 1981).
- Rubber boots, gloves and aprons are also recommended to prevent skin contact (GE 1979).
- The following chemical suit materials are recommended for protection against ammonia (EE-20): butyl, neoprene, chloropel and PVC (excellent resistance).
- Nonimpervious clothing which becomes contaminated with anhydrous ammonia or aqueous solutions of ammonia should be removed immediately and not reworn until the ammonia is removed from the clothing.
- Chemical showers and eye wash stations should be readily available to areas of use and spill situations (GE 1979).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where ammonia is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Gas concentration 100 ppm or less	Any chemical cartridge respirator with an ammonia cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.

Condition	Minimum Respiratory Protection* Required Above 50 ppm
300 ppm or less	A chemical cartridge respirator with a full facepiece and an ammonia cartridge(s).
500 ppm or less	A gas mask with a chin-style or a front- or back-mounted ammonia canister. Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm ** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against ammonia. Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.

** Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ammonia; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 500 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

9.1.8 Special Precautions for the Storage and Handling of Cylinders. Keep containers out of direct sunlight and away from heat. Store containers in a cool, well-ventilated, fire-resistant location away from oxidizing agents and combustible materials (GE 1979). Do not use copper, brass, bronze or galvanized steel in contact with ammonia. Cylinders should never be subjected to rough handling, dropping or bumping. Avoid dragging or sliding cylinders. Do not remove valve protection until ready to withdraw ammonia from the cylinder (MCA 1960).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment, materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study.

Ammonia Gas

Transfer Systems	B.F. Goodrich Acid and Chemical Tank-Truck Hose Goodall Chemical Hose Gates Chemical Handling Hose
Removal from Water	The Nold DeAerator

Liquefied Anhydrous Ammonia

Leak Plugging	Plug N'Dike™
Land Containment	"MSAR" Dike-Pak System
Removal from Water	EPA Mobile Physical-Chemical Treatment Trailers

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which can be useful to readers in planning spill response. Only those which meet these criteria are included and, thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most recent information.

10.1 Tanker Truck Spill (Personal Communication MOE 1982; Scarterfield 1981)

A tanker truck carrying approximately 10 900 kg of anhydrous ammonia overturned at a highway intersection due to disengagement of a wheel. An estimated 900 kg of ammonia vaporized from the safety relief valves before transfer of the contents into another tank truck was completed. The truck driver escaped without injuries.

Fire fighters, wearing Scott Air-packs, arrived at the scene and applied water spray to absorb the leaking vapours. Brisk winds of 40 km/h carried the escaping vapour over open farmland rather than over a densely populated area. The nearest dwelling, 300 m from the scene, was vacant. Evacuation was considered, but temporarily ruled out due to the direction of ammonia vapours over farmland only. Roads leading to the scene were blocked and the traffic was rerouted until the remaining ammonia was transferred into another tanker.

Due to a suspected high volume of ammonia-contaminated water (from water spraying), several attempts were made to contain the contaminated water at a nearby culvert. The earthen dyke failed and contaminated water escaped from the culvert into a storm sewer which discharged into a water stream. A few hours later, the dyke was reinforced and made secure by placing clay fill on the existing dyke and compacting it.

Response crews arrived at the scene 4 hours later to upright the tanker, which had disengaged itself from the truck cab during the accident. Inflatable air bags were initially used to upright the tanker but failed. Mechanical cranes were then used successfully. The remaining contents were transferred into another tanker and the wrecked tanker and cab hauled away.

Fire fighters estimated that approximately 545 000 L of water were used in spraying and knocking down the ammonia vapours. Samples of ammonia-contaminated water contained in the ditch had an ammonia concentration of 1165 mg/L. On the next day, approximately 310 000 L of ammonia-contaminated water were pumped from the drainage ditch and disposed of in gypsum ponds for further treatment. The dyke was removed and the soil was graded on the banks of the affected drainage ditch.

An estimated 235 000 L of ammonia-contaminated water discharged into the water stream (via culvert, storm sewer) during dyke failure. A fish kill, totalling approximately 75 000 to 100 000 fish, occurred in the affected stream. Cleanup crews recovered an estimated 4000 kg of dead fish from the stream. Three privately owned water wells in the vicinity of the accident scene were monitored. Analytical results indicated that the dissolved nutrient concentrations in the water were acceptable on the dates the samples were collected. Damage to cash crops in the vicinity of the accident scene was not evident. Air monitoring for ammonia vapours in houses near the spill site was carried out. Only low levels of ammonia were detected.

The authors feel that this incident illustrates the following points: anhydrous ammonia when released from pressure vessels often behaves as a "heavy" gas in that it moves along the ground; containment of contaminated waters at a spill site requires careful planning and construction to avoid further environmental damage; and rapid analytical techniques are necessary at spill scenes to make protection and countermeasures decisions.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Methods for the Detection of Ammonia in Air

11.1.1 Colourimetric - Azo Dye (APHA 1977). Ambient air containing 14 to 220 µg NH_3/m^3 (0.02 to 0.3 ppm), sampled at 1 to 2 L/min for 1 hour may be analyzed using this method. Ammonia is determined colourimetrically with an azo dye. Precision is ± 1.6 percent for the analytical method. Nitrite, hydrolyzable amino compounds and other N-compounds may interfere. For higher concentrations, an aliquot of the solution may be analyzed.

A measured volume of air is drawn through a prefilter to remove particulates and then through a dilute sulphuric acid solution (0.1 N H_2SO_4). The sample is reacted with 1 N sodium hypochlorite in the presence of an alkaline catalyst which consists of 160 g NaOH and 8 g NaBr in 1 L of water. Excess hypochlorite is destroyed with 0.2 m sodium arsenite. The nitrite produced is transformed into an azo dye by reaction with 5 mL of a buffered colour forming reagent. This is prepared by dissolving 10 g sulphanilamide, 126 g citric acid and 0.5 g naphthyl-1-ethylenediamine hydrochloride in 740 mL of 5 N H_2SO_4 and diluting to 1 L with water. Absorbance is measured at 545 nm in an appropriate spectrophotometer. An advantage of this method is that particulate ammonium compounds and ammonia may be analyzed separately.

11.1.2 Colourimetric - Nessler's Reagent (NIOSH 1977). The range of concentrations that can be determined by this method is 0.10 to 0.80 mg/10 L air sample or 20 to 135 ppm in air. Ammonia is determined colourimetrically using Nessler's reagent.

Several references were reviewed for the preparation of Nessler's reagent. The review indicates there is considerable leeway in the preparation with respect to amounts of materials and actual materials. The following was chosen as a representative recipe (Pierce 1958): dissolve 13 g of potassium iodide in 25 mL of ammonia-free water. Add, with constant stirring, a cold saturated solution of mercuric chloride ($HgCl_2$) until the precipitate that first forms no longer redissolves. Saturated mercuric chloride is prepared by dissolving 7 g in 100 mL of warm water or multiples thereof. Filter and add a solution of potassium hydroxide prepared by dissolving 55 g in 150 mL of water. Allow the precipitate of carbonate to settle and decant the clear solution. After addition of the base, dilute to about 250 mL, mix, and add a saturated solution of mercuric chloride drop by drop, keeping the solution well mixed, until a slight permanent precipitate is formed. Nessler's reagent is extremely toxic and should be handled with care. The reagent is ready to use.

A volume of air between 10 and 15 L is passed through 10 mL of 0.1 N sulphuric acid in a midget impinger. The sample is diluted to 50 mL with distilled water. Two mL of the Nessler's reagent are used for colour development with 1 mL of the sample solution diluted to 50 mL. The absorbance is measured after 10 minutes at 440 nm in a spectrophotometer using 1.0 cm cells. The method is quite sensitive but does not distinguish between free and combined ammonia. Particulate ammonium compounds and ammonia may, however, be determined separately by using appropriate filters.

11.1.3 Colourimetric - Indophenol (APHA 1977). The range of concentrations that can be determined by this method is 20 to 700 $\mu g/m^3$ (0.025 to 1 ppm) in air with a sampling time of 1 hour. Ammonia is determined colourimetrically using indophenol.

A measured volume of air is passed through 10 mL of 0.1 N sulphuric acid solution in a midget impinger. The sample is reacted with 5 mL of phenol solution and diluted to about 22 mL. The phenol solution is prepared by mixing 20 mL of 45 percent phenol solution with 1 mL of 2 percent sodium nitroprusside and diluted to 100 mL with water. Then 2.5 mL of a solution, prepared by mixing 30 mL of 0.1 N sodium hypochlorite and 30 mL of 6.75 M sodium hydroxide and diluting to 100 mL with water, is added to the 22 mL sample solution and this solution is diluted to 25 mL. The absorbance is measured at 630 nm in a spectrophotometer using 1.0 cm cells. Ammonium compounds suspended in particulate matter interfere if they are not removed by pre-filtration of the sampled air. Ferrous, chromous and manganous ions, if present in mg amounts, cause positive interference while copper ions cause negative interference in the analysis, but the addition of EDTA prevents these effects. Nitrite and sulphite interfere if they are present in 100-fold excess. Formaldehyde causes a negative interference of 10 to 15 percent. This method does not distinguish between free and combined ammonia. It is subject to interferences present in urban atmospheres.

11.1.4 Potentiometric Ion Electrode

11.1.4 Potentiometric Ion Electrode (ASTM 1980). The range of concentrations determined by this method is 10^{-6} to 1 M ammonia or 0.017 to 17 000 ppm NH_3. A measured volume of air is drawn through water. After sampling, the pH is adjusted to greater than 11 with sodium hydroxide. The ammonia gas sensing electrode is used to determine dissolved ammonia. Substances such as volatile amines and mercury, which are present in the urban atmosphere, interfere with the analysis. This is a fast and simple method for the determination of the presence of ammonia; however, since ionic activity rather than ionic concentration is determined, this is not the method of choice when the concentration must be known accurately.

11.2 Qualitative Method for the Detection of Ammonia in Air

Any of the above-mentioned quantitative colourimetric methods may be used for a rapid determination of the presence of ammonia using visual inspection rather than a spectrophotometer. The specific ion electrode described above is the fastest, most convenient method for the detection of the presence of ammonia.

11.3 Quantitative Methods for the Detection of Ammonia in Water

The form of ammonia most toxic to aquatic fauna is the unionized molecule. The currently available analytical methods for ammonia determine total ammonia as nitrogen (NH_3-N). The portion of total ammonia nitrogen that is unionized is a function of pH and temperature and is calculated by

$$f = 1/\left[10^{(pKa - pH)} + 1\right]$$

where

f = fraction of total ammonia in unionized state

pKa = 0.0901821 + (2729.92/T), negative log of dissociation constant for ammonia

pH = negative log of the hydrogen ion concentration

T = temperature, in degrees Kelvin (°C + 273.2)

A number of procedures for determining total ammonia nitrogen have been developed. Because pH and temperature play such an integral role in determining unionized ammonia concentration and because analytical variability is compounded in the calculation, precision and accuracy in pH and temperature measurement are also important. The following table of analytical methods contains a summary of the primary analytical reference, a summary of the chemistry, and the optimal concentration range. The methods described can be used on freshwater, wastewater and seawater, if care is exercised in overcoming inherent interferences (API 1981).

ANALYTICAL METHODS FOR DETERMINING AMMONIA NITROGEN (API 1981)

Procedure	Optimal Range (mg/L)	Interferences	
		Substance	Treatment
Colourimetric* phenate	0.010-2.000	Cations (Ca, Mg)	EDTA
		Salt (seawater)	Sodium-potassium tartrate
		Turbidity, colour	Filtration, centrifugation
		Urea, glycine, glutamic acid, cyanates, acetamide, volatile alkanes, ketones, aldehydes, alcohols, amines	Distillation
Colourimetric nesslerization	0.020-1.000	Turbidity, color	Filtration, centrifugation
		Aromatic and aliphatic amines, cyanate, ketones, aldehydes, alcohols	Z_nSO_4 Distillation
		Cations	EDTA
		Residual chlorine	Sodium thiosulphate
Titrimetric	1.0-25.0	Turbidity, color	Filtration, centrifugation
		Aromatic and aliphatic amines, cyanate, ketones, aldehydes, alcohols	Distillation
		Cations	EDTA
		Residual chlorine	Sodium thiosulphate
Potentiometric	0.05-1,400	Volatile amines Mercury	Distillation

* Not described in Section 11.1.

Field samples for ammonia determination must be preserved by adding 2 mL of concentrated sulphuric acid and holding at 4°C until analyzed. Even so, ammonia must be determined within 24 hours of collection to ensure representative results. This is mandatory because ammonia is a volatile and reactive compound. It may volatilize from collected samples or it may be oxidized to nitrite and then nitrate. It may also be assimilated by phytoplankton entrained in a sample bottle.

11.3.1 **Distillation.** The ammonia sample must be distilled at pH 9.5 prior to the final analysis. This procedure will eliminate or significantly reduce many materials that may interfere with the determination. For example, glycine, urea, glutamic acid, cyanates and acetamide spontaneously hydrolyze very slowly. Glycine, hydrozine and some amines react with Nessler reagent to cause a positive interference. Ketones, aldehydes, alcohols and some amines react with Nessler reagent to form an interfering green color and turbidity. A 500 mL sample is buffered to pH 9.5 with borate buffer to reduce hydrolysis of cyanates and organic nitrogen compounds. Some pH adjustment with 6 N sodium hydroxide may be required. The distillate is collected in boric acid if ammonia is to be determined by nesslerization or titration or in sulphuric acid if the phenate method is to be used. The former is prepared by dissolving 20 g of boric acid in 1 L of water.

11.3.2 **Titrimetric** (ASTM 1980). Ammonia is determined titrimetrically using standard 0.02 N sulphuric acid to a methyl red/methylene blue endpoint. The ammonia concentration is calculated stoichiometrically based on the volume of titrant used. This type of analysis, even after distillation, has a potential to suffer from interferences. Carry-over caustic aerosols and degradation of volatile amines will interfere with the titration. The procedure should never be used to determine ammonia directly.

11.3.3 **Colourimetric Nesslerization.** Ammonia reacts with mercuric iodide and potassium iodide (Nessler reagent) in sodium hydroxide solution to produce a yellow-brown colour, the intensity of which is proportional to the ammonia concentration in the sample. The intensity of the colour complex may be determined spectrophotometrically at 450 to 500 nm or by visual comparison using matched colour comparison tubes (Nessler tubes).

Turbidity, colour, and excessive concentrations of calcium, iron, magnesium, and sulphide interfere with direct nesslerization. The distillation described above will remove many of these interferences; additonal cation removal can be accomplished by addition of EDTA. Because colour and turbidity interfere so strongly, it is recommended that direct nesslerization be used only on drinking water samples. Residual chlorine must be removed by pretreatment with sodium thiosulphate.

A volume of distillate containing not more than 0.1 mg ammonia nitrogen is diluted to 50 L. If it is turbid, it must be clarified with zinc sulphate and sodium hydroxide solutions. It is mixed, 1 mL of the Nessler's reagent is added, and the absorbance is measured at 425 nm in a suitable spectrophotometer. See Section 11.1.2 for the preparation of Nessler's reagent. The method is applicable to all types of water and is specific for ammonia nitrogen rather than for organic nitrogen.

11.3.4 Potentiometric Non-specific Electrode (ASTM 1980). Concentrations between 10^{-6} and 1 M ammonia or 0.017 to 17 000 ppm can be determined by this method.

Ionized ammonia in a water sample is converted to gaseous ammonia by raising the pH above 11. The ammonia thus formed diffuses through a hydrophobic gas-permeable membrane on the electrode face. The diffused ammonia alters the pH of the electrode internal reference solution. The pH change is measured by the electrode and the potential change indicated on a pH or specific-ion meter. The change in potential is proportional to the ammonia concentration.

Volatile amines hydrolyze at high pH and thus serve as a positive interference in this procedure. Mercury interferes by forming strong complexes with ammonia. The electrode membrane degrades rapidly when exposed for long periods of time to industrial effluents containing high concentrations of phenolic compounds. Although ammonia nitrogen can be determined directly by electrode, it is nevertheless desirable to distill samples to minimize interference.

A representative sample is collected and the pH is adjusted to greater than 11 with sodium hydroxide. The ammonia gas sensing electrode is used. This is a fast and simple method for the determination of the presence of ammonia but since ionic activity rather than ionic concentration is determined, this method is not the method of choice when the concentration must be known accurately.

11.4 Qualitative Method for the Detection of Ammonia in Water

Ammonia may be detected in water by placing five drops of the water in a beaker, adding 3 N potassium hydroxide to make it alkaline, then covering the beaker with a watch glass to which adheres a strip of moistened red litmus paper. If, when the solution is warmed gently, the litmus paper turns from red to blue, ammonia is present (Gilreath 1952). Volatile amines will also produce the same colour change.

11.5 Quantitative Method for the Detection of Ammonia in Soil

Field samples for ammonia determination must be preserved by adding 2 mL of concentrated sulphuric acid and holding at 4°C until analyzed. See Section 11.3. If physically absorbed ammonia is not important, the above procedure is unnecessary. Chemically sorbed material can be extracted by treatment with potassium chloride solution.

11.5.1 Distillation (Hesse 1972; ASTM 1979). Ammonia at concentrations of up to 0.5 ppm in the extracting solution may be determined using the colourimetric method, or up to 5 ppm in the extracting solution using the titrimetric method. A known weight of soil is shaken for 2 hours with neutral 2 M potassium chloride solution and filtered. An aliquot of the filtrate is treated with a base, sometime sodium hydroxide but usually magnesium oxide. The mixture is distilled into a boric acid solution and determined acidimetrically or colourimetrically as described in Sections 11.3.2 and 11.3.3, respectively. An acidified salt solution is not suitable for extraction of ammonia from soil if nitrate, nitrite or organic nitrogen are present since they will interfere.

11.6 Qualitative Method for the Detection of Ammonia in Soil

A fast test for the presence of ammonia involves reacting the extract prepared as in Section 11.4 with 3 N potassium hydroxide, gently heating and noting the change in the colour of litmus paper from red to blue (Gilreath 1954). Volatile amines will also produce this change.

12 REFERENCES AND BIBLIOGRAPHY

12.1 References

AA 1970: Compressed Gas Association Inc., Anhydrous Ammonia, New York, New York. (1970).

AAR 1981: BDM Corporation, The AAR Hazardous Materials Data Base, Prepared for the Association of American Railroads, Parts I and II, McLean, Virginia. (May, 1981).

Alabaster 1979: Alabaster, J.S., Shurben, D.G., Knowles, G., "The Effect of Dissolved Oxygen and Salinity on the Toxicity of Ammonia to Smolts of Salmon, Salmo Salar", J. Fish. Biology, Vol. 15, No. 6, pp. 705-712. (1979).

Ammonia 1979: National Research Council (United States), Ammonia, Committee on Medical and Biological Effects of Environmental Pollutants, Division of Medical Sciences, Assembly of Life Sciences, University Park Press, Baltimore, Maryland. (1979).

APHA 1975: American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1976 Standard Methods for the Examination of Water and Wastewater, 14 Edition, APHA, Washington, D.C. (1975).

APHA 1977: Katz, M., Methods of Air Sampling and Analysis, Second Edition, American Public Health Association, Washington, D.C., Method 402. (1977).

API 1981: American Petroleum Institute, The Sources, Chemistry, Fate and Effects of Ammonia in Aquatic Environments, Washington, D.C. (1981).

APM 1967: U.S. Department of Health, Education, and Welfare, Air Pollution Abatement Manual, Cincinnati, Ohio. (1967).

Arillo 1981: Arillo, A., Margiocco, C., Melodia, F., et al., "Ammonia Toxicity Mechanism in Fish: Studies on Rainbow Trout (Salmo Gairdneri Rich.)", Ecotoxicology and Environmental Safety, Vol. 5, pp. 316-328. (1981).

Armstrong 1978: Armstrong, D.C., Chippendale, D., Knight, A.W., Colt, J.E., "Interaction of Ionized and Un-ionized Ammonia on Short-term Survival and Growth of Prawn Larvae, Macrobrachium Rosenbergii", Biol. Bull., Vol. 154, pp. 15-31. (1978).

ASS: Atlas Steel, Atlas Stainless Steels, Toronto, Ontario. Not dated.

ASTM 1979: American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31: Water, ASTM, Philadelphia, Pennsylvania, D1426-79, D1192-70, D3370. (1979).

ASTM 1980: American Society for Testing and Materials, Compilation of Odor and Taste Threshold Values Data, ASTM, Philadelphia, Pennsylvania, ASTM Data Series DS-48A. (1980).

Ball 1967: Ball, I.R., "The Relative Susceptibilities of Some Species of Freshwater Fish to Poisons. I. Ammonia", Water Res. Vol. 1, pp. 767-775. (1967).

Braker 1977: Braker, W., Mossman, A.L., Effects of Exposure to Toxic Gases - First Aid and Medical Treatment, Second Edition. (1977).

Braley 1980: Braley, G.K., "Several Remedies for the Treatment of Spillages of Liquid Hazardous Chemicals", Proceedings of the 1980 National Conference on Control of Hazardous Material Spills. (May, 1980).

Bretherick 1979: Bretherick, L., Handbook of Reactive Chemical Hazards, Second Edition, Butterworths, London, England. (1979).

Brownell 1980: Brownell, C.L., "Water Quality Requirements for First Feeding in Marine Fish Larvae. 1. Ammonia, Nitrite, Nitrate", J. Exper. Mar. Biol. Ecol., Vol. 44 No. 2-3, pp. 269-284. (1980).

Buckley 1978: Buckley, J.A., "Acute Toxicity of Un-ionized Ammonia to Fingerling Coho Salmon", Prog. Fish Cult., Vol. 40, pp. 30-32. (1978).

CBG 1980: Southam Business Publications Ltd., "1981 Chemical Buyers' Guide", Canadian Chemical Processing, Vol. 64, No. 9, Don Mills, Ontario. (December, 1980).

CCP 1980: "Ammonia Plants More Efficient", Canadian Chemical Processing, Vol. 64, No. 7, p. 10. (15 October 1980).

CCP 1982(a): "Ambitious Plans for BC Gas", Canadian Chemical Processing, Vol. 66, No. 1, p. 14. (February, 1982).

CCP 1982(b): "More Ammonia PE for CIL", Canadian Chemical Processing, Vol. 66, No. 2, p. 14. (March, 1982).

CCPA 1982: Canadian Chemical Producers' Association, Ottawa, Ontario, Private Communication. (1982).

CDS 1967: National Association of Corrosion Engineers, Corrosion Data Survey, Houston, Texas. (1967).

CE 1978: Heller, H., Aqueous Ammonia Liquid/Vapour Composition Nomograph, Chemical Engineering, McGraw-Hill Book Company, New York, New York, pp. 131-132. (December, 1978).

CG-D-16-77: Drake, E., et al., A Feasibility Study of Response Techniques for Discharges of Hazardous Chemicals that Disperse Through the Water Column, U.S. Coast Guard, Washington, D.C., CG-D-16-77. (July, 1976).

CG-D-38-76: Bauer, W.H., Borton, D.N., et al., Agents, Methods and Devices for Amelioration of Discharge of Hazardous Chemicals on Water, Rensselaer Polytechnic Institute for the U.S. Coast Guard, Washington, D.C., CG-D-38-76. (August 1975).

Chem. Eng. 1974: Yaws, C.L., "Physical and Thermodynamic Properties", Chemical Engineering, Vol. 81, No. 25, p. 91. (25 November 1974).

CHRIS 1974: U.S. Department of Transportation, Coast Guard, CHRIS Hazard Assessment Handbook, Washington, D.C., CG-446-3. (April, 1974).

CHRIS 1978: U.S. Department of Transportation, Coast Guard, Chemical Hazards Response Information System (CHRIS), Washington, D.C. (1978).

Colt 1976: Colt, J., Tchobanoglous, G., "Evaluation of the Short-term Toxicity of Nitrogeneous Compounds to Channel Catfish, 'ctalurus Punctatus", Aquaculture, Vol. 8, pp. 209-224. (1976).

Colt 1978: Colt, J., Tchabanoglous, G., "Chronic Exposure of Channel Catfish, Ictalurus Punctatus, to Ammonia: Effects on Growth and Survival", Aquaculture, Vol. 15, pp. 353-372. (1978).

Corpus 1983: Corpus Information Services Ltd., "Ammonia", Chemical Product Profiles, Don Mills, Ontario. (1983).

Cotton 1972: Cotton, F.A., Wilkinson, G., Advanced Inorganic Chemistry, Interscience Publishers, New York, New York. (1972).

CRC 1982: Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, 60th Edition, Chemical Rubber Publishing Company, Cleveland, Ohio. (1982).

DCRG 1972: Dow Chemical Company, Dow Chemical Resistance Guide for Dow Plastic Lined Piping Products, Midland, Michigan. (1972).

Dillon 1982: M.M. Dillon, Survey of Countermeasures Systems for Hazardous Material Spills, Environment Canada, Ottawa, Canada. (1982).

Doc. TLV 1980: American Conference of Governmental Industrial Hygienists (ACGIH), Documentation of Threshold Limit Values, Fourth Edition, Cincinnati, Ohio. (1980).

Dow ERIS 1981: Dow Chemical Canada Inc., "Ammonia, Anhydrous Technical", Emergency Response Information Sheet, Sarnia, Ontario. (April, 1981).

Dow PPS 1972: Dow Chemical Company, Dow Plastic Lined Piping Systems, Midland, Michigan. (1972).

DPPED 1967: DOM-X, DOM-X Plastic Pipe Engineering Data, Toronto, Ontario. (1967).

Dreisbach 1980: Dreisbach, R.H., Handbook of Poisoning: Prevention, Diagnosis, and Treatment, Tenth Edition, Lange Medical Publications, Los Altos, California. (1980).

EAG 1978: U.S. Department of Transportation, Emergency Action Guide for Selected Hazardous Materials, Research and Special Programs Administration, Materials Transportation Bureau, Washington, D.C. (1978).

EE-20: Buchan, Lawton, Parent Ltd., A Survey of Self-contained Breathing Apparatus and Totally-encapsulated Chemical Protection Suits, Unedited Version. Not dated.

EST 1978: Environmental Science and Technology. (1978).

EPA 1979: Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratories, Cincinnati, Ohio. (1979).

EPA 440/9-75-009: Environmental Protection Agency, Supplement to Development Document: Hazardous Substances Regulations, Section 311 Federal Water Pollution Control Act, U.S. Environmental Protection Agency, Office of Water and Standards, Washington, D.C., EPA 440/9-75-009. (November, 1975).

EPA 600/2-76-109: Gupta, K., Development of a Mobile Treatment System for Handling Spilled Hazardous Materials, U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, EPA 600/2-76-109. (July, 1976).

EPA 600/2-76-300: Vrolyk, J.J., et al., Prototype System for Plugging Leaks in Ruptured Containers, U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, EPA 600/2-76-300. (December, 1976).

EPA 600/2-77-227: Huibregtse, K.R., et al., Manual for the Control of Hazardous Material Spills - Volume One - Spill Assessment and Water Treatment Techniques, U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, EPA 660/2-77-227. (November, 1977).

EPA 600/2-80-076: Hatayama, H.K., Chen, J.J., deVera, E.R., Stephens, R.D., Storm, D.L., A Method for Determining the Compatibility of Hazardous Wastes, U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Office of Research and Development, Cincinnati, Ohio. (April, 1980).

EPA 600/8-80-042E: Environmental Protection Agency, Treatability Manual, Volume V, Summary, U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., EPA 600/8-80-042E. (July, 1980).

EPA 670/2-75-042: Pilie, R.J., et al., Methods to Treat, Control and Monitor Spilled Hazardous Materials, U S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, EPA 670/2-75-042. (June, 1975).

Epifanio 1975: Epifanio, L.E., Srna, R.F., "Toxicity of Ammonia, Nitrate Ion, and Orthophosphate to Mercenaria Mercenaria and Crassostrea Virginica", Mar. Biol. Vol. 33, pp. 241-246. (1975).

Erco HCM 1981: Erco Industries Limited, Hazards of Chemicals Manual, Islington, Ontario. (March, 1981).

ERG 1980: U.S. Department of Transportation, Hazardous Materials, 1980 Emergency Response Guidebook, Research and Special Programs Administration, Materials Transportation Bureau, Washington, D.C. (1980).

Evans 1979: Evans, J.W., The Construction and Use of a Continuous-flow Bioassay Apparatus to Determine a Preliminary Un-Ionized Ammonia 96-hour LC_{50} for the Crayfish, (Orconectes Nais), Master's thesis, Kansas State University. (1979).

GE 1979: General Electric Company, Material Safety Data Sheets, Material Safety Information Services, Schenectady, New York. (November, 1979).

GF: GF Plastic Systems Inc., GF Plastic Systems, Santa Ana, California. Not dated.

Gilreath 1954: Gilreath, E.S., Qualitative Analysis Using Semimicro Methods, McGraw Hill Book Company, New York, New York, p. 221. (1954).

Gosselin 1976: Gosselin, R.E., Hodge, H.C., Smith, R.P., Gleason, M.N., Clinical Toxicology of Commercial Products, 4th Edition, The Williams & Wilkins Co. (1976).

GPP: Uniroyal, Guide to Polymer Properties, Uniroyal Inc., Mishawaka, Indiana. Not dated.

Hazel 1971: Hazel, C.R., Thomsen, W., Meith, S.J., "Sensitivity of Striped Bass and Stickleback to Ammonia in Relation to Temperature and Salinity", Calif. Fish Game, Vol. 57, pp. 138-153. (1971).

Hazel 1979: Hazel, R.H., Burkhead, C.E., Huggins, D.G., The Development of Water Quality Criteria for Ammonia and Total Residual Chlorine for the Protection of Aquatic Life in Two Johnson County, Kansas, Streams, U.S. Department of the Interior, Office of Water Research and Technology, Washington, D.C. (1979).

HCG 1981: Compressed Gas Association, Inc., Handbook of Compressed Gases, Second Edition, Van Nostrand Reinhold Company, New York, New York. (1981).

Herbert 1964: Herbert, D.W.M., Shurben, D.S., "The Toxicity to Fish of Mixtures of Poisons. I. Salts of Ammonia and Zinc", Ann. Appl. Biol., Vol. 53, pp. 33-41. (1964).

Herbert 1965: Herbert, D.W.M., Shurben, D.S., "The Susceptibility of Salmonid Fish to Poisons Under Estuarine Conditions. II. Ammonia Chloride", Int. J. Air Water Pollut., Vol. 9, pp. 89-91. (1965).

Hesse 1972: Hesse, P.R., A Textbook of Soil Chemical Analysis, Chemical Publishing Co. Inc., New York, New York, p. 168. (1972).

HIS 1969: Hydraulic Institute, Hydraulic Institute Standards, 12th Edition, New York, New York. (1969).

ILO 1980: International Labour Organization, Occupational Exposure Limits for Airborne Toxic Substances, Second (Revised) Edition, Geneva, Switzerland. (1980).

ITII 1981: International Technical Information Institute, Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazard Data, Japan. (1981).

JANAF 1971: Stull, D.R., Prophet, H., JANAF Thermochemical Tables, Second Edition, U.S. National Bureau of Standards, Office of Standard Reference Data, Washington, D.C. (June, 1971).

Jolly 1964: Jolly, W.L., The Inorganic Chemistry of Nitrogen, W.A. Benjamin Inc., New York, New York. (1964).

JSSV 1979: Jenkins Brothers, Jenkins Corrosion Resistant Stainless Steel Valves, New York, New York. (1979).

Jude 1973: Jude, D.J., Sublethal Effects of Ammonia and Cadmium on Growth of Green Sunfish, Ph. D. dissertation, Michigan State University. (1973).

Kane 1979: Kane, L.E., Barrow, C.S., Alarie, Y., "A Short-term Test to Predict Acceptable Levels of Exposure to Airborne Sensory Irritants", American Industrial Hygiene Association Journal, Vol. 40, No. 3, p. 207. (1979).

Kirk-Othmer 1978: Grayson, M., Eckroth, D. (ed.), Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, John Wiley & Sons Inc., New York, New York. (1978).

Kirk-Othmer 1980: Grayson, M., Eckroth, D. (ed.), Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 2, John Wiley & Sons Inc., New York, New York. (1980).

Kormondy 1969: Kormondy, E.J., Concepts of Ecology, Prentice-Hall Inc., Englewood Cliffs, New Jersey. (1969).

Lefèvre 1980: Lefèvre, M.J., Becker, E.O., First Aid Manual for Chemical Accidents -For Use with Nonpharmaceutical Chemicals, Dowden, Hutchinson, and Ross Inc., Stroudsburg, Pennsylvania. (1980).

Leonardos 1969: Leonardos, G., Kendall, D., Bernard, N., "Odor Threshold Determinations of Odorant Chemicals", Journal of Air Pollution Control Association, Vol. 19, No. 2, p. 91. (1969).

Linde 1981: Linde Specialty Gases, Union Carbide Canada Limited, Oakville, Ontario. (1981).

Matheson 1966: Matheson Company Inc., Matheson Gas Data Book, East Rutherford, New Jersey. (1966).

Matheson 1980: Braker, W., Mossman, A.L. (ed.), Matheson Gas Data Book, Matheson Company Inc., Lyndhurst, New Jersey. (1980).

MCA 1947: Manufacturing Chemists Association, Aqua Ammonia, Washington, D.C. (1947).

MCA 1960: Manufacturing Chemists Association, Anhydrous Ammonia, Washington, D.C. (1960).

MWPP 1978: Rehau, Mechan-O-Joint Water Pressure Pipe and Fittings, Montreal, Quebec. (1978).

NFPA 1978: National Fire Protection Association, Fire Protection Guide on Hazardous Materials, Seventh Edition, Boston, Massachusetts. (1978).

NIOSH 1974: National Institute for Occupational Safety and Health, Criteria for a Recommended Standard - Occupational Exposure to Ammonia, U.S. Department of Health, Education and Welfare, Cincinnati, Ohio, NIOSH 74-136. (1974).

NIOSH 1977: National Institute for Occupational Safety and Health, Manual of Analytical Methods, Second Edition, Vol. 1, Cincinnati, Ohio. (April, 1977).

NIOSH Guide 1978: U.S. Department of Health, Education and Welfare, Pocket Guide to Chemical Hazards, U.S. Department of Health, Education, and Welfare, and U.S. Department of Labor, Washington, D.C. (1978).

NIOSH/OSHA 1981: U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health (NIOSH), U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), Occupational Health Guidelines for Chemical Hazards, NIOSH Publication No. 81-123. (1981).

NSC 1979: National Safety Council, Data Sheet for Anhydrous Ammonia, National Safety Council, Chicago, Illinois, 1-251-79. (Revised 1979).

OHM-EPWE 1968: Oil and Hazardous Materials - Emergency Procedures in the Water E[illegible] S Department of Interior, Edison, New Jersey. (October, 1968).

OHM-TADS 1977: Oil and Hazardous Materials Technical Assistance Data System, U.S. Environmental Protection Agency, Oil and Special Materials Control Division, Office of Water Program Operations, Washington, D.C., Microfiche. (1977).

OHM-TADS 1981: Oil and Hazardous Materials Technical Assistance Data System, U.S. Environmental Protection Agency, Oil and Special Materials Control Division, Office of Water Program Operations, Washington, D.C. (1981).

O.I. 1970: Oceanology International. (October, 1970).

Ontario E.P. Act 1971: Ontario Ministry of the Environment, "The Environmental Protection Act, Statutes of Ontario 1971", Chapter 86, as amended; and Regulation 15 (General) as amended. (1971).

Orion: Orion Research Technical Literature, Method 502, Cambridge, Massachusetts. Not dated.

Patty 1981: Clayton, G.D., Clayton, F.E. (ed.), Patty's Industrial Hygiene and Toxicology, Vols. 2A, 2B, Third Revised Edition, John Wiley and Sons Canada Limited, Toronto, Ontario. (1981).

Perry 1973: Perry, R.H., Chilton, C.H. (ed.), Chemical Engineer's Handbook, Fifth Edition, McGraw-Hill Book Company, New York, New York. (1973).

Personal Communication with MOE 1982: Personal Communication, Ontario Ministry of the Environment, Sarnia, Ontario. (19 January 1982).

Peterson 1977: Peterson, S.E., Schutsky, R.M., Rosage, T.F., Supplementary Material on Toxicity of Ammonia to Selected Fishes of the Conestoga River, Lancaster County, Ichthyological Associates Inc., Unpublished. (1977).

Pierce 1958: Pierce, W.C., Sawyer, D.T., Haenisch, E.L., Quantitative Analysis, 4th Edition, John Wiley & Sons, New York. (1958).

PNL 1981: Brenchley, D.L., Assessment of Research and Development Needs in Ammonia Safety and Environmental Control, Pacific Northwestern Laboratory, PNL-4006, UC-11. (1981).

Proctor 1978: Proctor, N.H., Hughes, J.P., Chemical Hazards of the Workplace, J.B. Lippincott Company, Toronto, Ontario. (1978).

Raj 1974: Raj, P.P.K., Lakekar, A.S., Assessment Models in Support of Hazard Assessment Handbook, Prepared for the Department of Transportation, U.S. Coast Guard, Washington, D.C., p. 238. (January, 1974).

Raj 1978: Raj, P.P.K., Reid, R.C., "Fate of Liquid Ammonia Spilled onto Water", Environmental Science and Technology, Vol. 12, No. 134, pp. 1422-1425, American Chemical Society, Washington, D.C. (December, 1978).

Reddy 1979: Reddy, N.A., Menon, N.R., "Effects of Ammonia and Ammonium on Tolerance and Byssogenesis in Perna Viridis", Marine Ecology - Progress Series, Vol. 1, No. 4, pp. 315-322. (1979).

Resplandy 1969: Resplandy, A., "Etude expérimentale des propriétés de l'ammonia conditionnant les mesures à prendre pour la sécurité du voisinage des stockages industriels Chemi et Industrie", Genie Chimique, Vol. 102, pp. 691-702. (1969).

Robinette 1976: Robinette, H.R., "Effect of Selected Sublethal Levels of Ammonia on the Growth of Channel Catfish (Ictalurus Punctatus)", Prog. Fish. Cult., Vol. 38, pp. 26-29. (1976).

Robbins 1977: Robbins, T.W., Peterson, S.E., Schutsky, R.M., Rosage, T.F., Toxicity of Ammonia to Selected Fishes of the Conestoga River, Lancaster County, Ichthyological Associates, Inc., Unpublished. (1977).

Robinson-Wilson 1[illegible]5: Robinson-Wilson, E.F., Seim, W.K., "The Lethal and Sublethal Effects of a Zirconium Process Effluent on Juvenile Salmonids", Water Resour. Bull., Vol. 11, No. 5, pp. 975-986. (1975).

Rosage 1979: Rosage, T.F., Schutsky, R.M., Rapp, K.M., "Toxicity of Un-Ionized Ammonia to the Spotfish Shiner (Notropis Spilopterus)", Proc. Pa. Acad. Sci., Vol. 53, pp. 39-42. (1979).

Roseboom 1977: Roseboom, D.P., Richey, D.L., Acute Toxicity of Residual Chlorine and Ammonia to Some Native Illinois Fishes, Illinois State Water Survey, Illinois, ISWS/RI-85/77. (1977).

Rosenstock 1977: Rosenstock, H.M., Draxl, K., Steiner, B., Herron, J.T., Energetics of Gaseous Ions, National Bureau of Standards, Washington, D.C. (1977).

RTDCR 1974: Regulations for the Transportation of Dangerous Commodities by Rail, Canadian Transport Commission, published by Supply and Services Canada, Ottawa, Ontario. (1974).

RTECS 1979: Lewis, R.J., Tatken, R.L., Registry of Toxic Effects of Chemical Substances, 1979, Vols. 1 and 2, National Institute for Occupational Safety and Health (NIOSH), Cincinnati, Ohio. (September, 1980).

RTECS (on-line) 1981: National Institute for Occupational Safety and Health, Registry of Toxic Effects of Chemical Substances, U.S. Department of Health and Human Services, Microfiche. (October, 1981).

Rubin 1977: Rubin, A.J., Elmaraghy, G.A., "Studies on the Toxicity of Ammonia, Nitrate and Their Mixtures to Guppy Fry", Water Res., Vol. 11, pp. 927-935. (1977).

Sax 1979: Sax, N.I., Dangerous Properties of Industrial Materials, Fifth Edition, Van Nostrand Reinhold Company, New York, New York. (1979).

Scarterfield 1981: Scarterfield, J., Ministry Investigation of Tanker Truck Accident Involving the Escape of Anhydrous Ammonia Vapour, June 15, 1981, Ministry of the Environment, Industrial Abatement Section, Sarnia, Ontario. (1981).

Scott 1979: Scott's Industrial Directory of Ontario Manufacturers, 12th Edition, Penstock Directories Limited, Oakville, Ontario. (1979).

Shreve 1977: Shreve, R.N., Brink, J.A., Chemical Process Industries, Fourth Edition, McGraw-Hill Book Company Inc., New York, New York. (1977).

Sisler 1961: Sisler, H.H., Chemistry in Non-aqueous Solvents, Reinbold Publishing Corp., New York, New York. (1967).

Smart 1978: Smart, G., "Investigations of the Toxic Mechanism of Ammonia to Fish: Gas Exchange in Rainbow Trout (Salmo Gairdneri) Exposed to Acutely Lethal Concentrations", Journal of Fish Biology, Vol. 12, pp. 93-104. (1978).

Spehar 1981: Spehar, R.L., Lemke, A.E., et al., "Effects of Pollution on Freshwater Fish", Journal of Water Pollution Control Federation, Vol. 53, No. 6, pp. 1028-1076. (June, 1981).

Stevenson 1977: Stevenson, T.J., The Effect of Ammonia, pH and Salinity on the White Perch Morone Americana, Ph.D. dissertation, University of Rhode Island. (1977).

Sullivan 1969: Sullivan, R.J., Air Pollution Aspects of Odorous Compounds, U.S. Department of Commerce, PB 188089. (1969).

TCM 1979: General American Transportation Corporation, Tank Car Manual, Chicago, Illinois. (May, 1979).

TDGC 1980: Transport Canada, Transportation of Dangerous Goods Code, Vol. 1 (Lists), Vol. 2, Ottawa, Ontario. (June, 1980).

Thurston 1978: Thurston, R.V., Russo, R.C., Smith, C.E., "Acute Toxicity of Ammonia and Nitrate to Cutthroat Trout Fry", Transactions of the American Fisheries Society, Vol. 107, No. 2, pp. 361-368. (1978).

Thurston 1981: Thurston, R.V., Russo, R.C., "Ammonia Toxicity to Fishes. Effect of pH on the Toxicity of the Un-ionized Ammonia Species", Environmental Science and Technology, Vol. 15, No. 7, pp. 838-840. (July, 1981).

TLV 1983: American Conference of Governmental Industrial Hygienists, TLV®s Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1983-84, Cincinnati, Ohio. (1983).

Todd 1970: Todd, D.K., The Water Encyclopedia, Maple Press, New York, New York. (1970).

Tommasso 1980: Tommasso, J.R., Goudie, G.A., Simco, B.A., Davis, K.B., "Effects of Environmental pH and Calcium on Ammonia Toxicity in Channel Catfish", Trans. Am. Fish. Soc., Vol. 109, pp. 229-234. (1980).

TOX TIPS 1981: Toxicology Testing in Progress, Sponsored by Toxicology Information Subcommittee, DHEW Committee to Coordinate Environmental and Related Programs, Available from the National Library of Medicine and NTIS. (1981).

TPS 1978: GSR Fluid Handling, Thermoplastic Piping Systems, Sun Valley, California. (1978).

Ullmann 1974: Bartholome, E., Biekert, E.J., Hellmann, H. Ley, H. (ed.) Ullmanns Encyklopaedie der technischen Chemie, Verlag Chemie, Weinheim. (1974).

Verschueren 1977: Verschueren, K., Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Company, New York, New York. (1977).

Water Management Goals 1978: Ontario Ministry of the Environment, Water Management Goals, Policies, Objectives and Implementation Procedures for the Ministry of the Environment, Toronto, Ontario. (November, 1978).

Wickens 1976: Wickens, J.F., "The Tolerance of Warmwater Prawns to Recirculated Water", Aquaculture, Vol. 9, pp. 19-37. (1976).

WQC 1963: McKee, J.E., Wolf, H.W., Water Quality Criteria, Second Edition, Resources Agency of California, State Water Quality Control Board. (1963).

WQC 1972: National Academy of Sciences, Water Quality Criteria 1972, A Report of the Committee on Water Quality Criteria, Environmental Studies Board, National Academy of Sciences, Washington, D.C., p.p. 186-188, 242, 450-461. (1972).

WQCEFF 1973: "Water Quality Criteria for European Freshwater Fish", Water Research, Vol. 7, pp. 1011-1022. (1973).

WQS 1979: McNeily, R.N., Neimans, V.P., Dwyer, L., Water Quality Sourcebook: A Guide to Water Quality Parameters, Inland Waters Directorate, Water Quality Branch, Environment Canada, Ottawa, Canada. (1979).

Yopp 1974: Yopp, J.H., Schmid, W.E., Holst, R.W., Determination of Maximum Permissible Levels of Selected Chemicals that Exert Toxic Effects on Plants of Economic Importance in Illinois, NTIS, Springfield, Virginia, PB-327-654. (August, 1974).

12.2 Bibliography

Alabaster, J.S., Shurben, D.G., Knowles, G., "The Effect of Dissolved Oxygen and Salinity on the Toxicity of Ammonia to Smolts of Salmon, Salmo Salar", J. Fish. Biology, Vol. 15, No. 6, pp. 705-712. (1979).

"Ambitious Plans for BC Gas", Canadian Chemical Processing, Vol. 66, No. 1, p. 14. (February, 1982).

American Conference of Governmental Industrial Hygienists (ACGIH), Documentation of Threshold Limit Values, Fourth Edition, Cincinnati, Ohio. (1980).

American Conference of Governmental Industrial Hygienists, TLV®s Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1983-84, Cincinnati, Ohio. (1983).

American Petroleum Institute, The Sources, Chemistry, Fate and Effects of Ammonia in Aquatic Environments, Washington, D.C. (1981).

American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1976 Standard Methods for the Examination of Water and Wastewater, 14th Edition, APHA, Washington, D.C. (1975).

American Society for Testing and Materials, Compilation of Odor and Taste Threshold Values Data, ASTM, Philadelphia, Pennsylvania, ASTM Data Series DS-48A. (1980).

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31: Water, ASTM, Philadelphia, Pennsylvania, D1426-79, D1192-70, D3370. (1979).

"Ammonia Plants More Efficient", Canadian Chemical Processing, Vol. 64, No. 7, p. 10. (15 October 1980).

Arillo, A., Margiocco, C., Melodia, F., et al., "Ammonia Toxicity Mechanism in Fish: Studies on Rainbow Trout (Salmo Gairdneri Rich.)", Ecotoxicology and Environmental Safety, Vol. 5, pp. 316-328. (1981).

Armstrong, D.A., Chippendale, D., Knight, A.W., Colt, J.E., "Interaction of Ionized and Un-ionized Ammonia on Short-term Survival and Growth of Prawn Larvae, Macrobrachium Rosenbergii", Biol. Bull., Vol. 154, pp. 15-31. (1978).

Atlas Steel, Atlas Stainless Steels, Toronto, Ontario. Not dated.

Ball, I.R., "The Relative Susceptibilities of Some Species of Freshwater Fish to Poisons. I. Ammonia", Water Res., Vol. 1, pp. 767-775. (1967).

Bartholome, E., Biekert, E.J., Hellmann, H. Ley, H. (ed.), Ullmanns Encyklopaedie der technischen Chemie, Verlag Chemie, Weinheim. (1974).

Bauer W.H., Borton, D.N., et al., Agents, Methods and Devices for Amelioration of Discharge of Hazardous Chemicals on Water, Rensselaer Polytechnic Institute for the U.S. Coast Guard, Washington, D.C., CG-D-38-76. (August, 1975).

BDM Corporation, The AAR Hazardous Materials Data Base, Prepared for the Association of American Railroads, Parts I and II, McLean, Virginia. (May, 1981).

Braker, W., Mossman, A.L., Effects of Exposure to Toxic Gases - First Aid and Medical Treatment, Second Edition. (1977).

Braker, W., Mossman, A.L. (ed.), Matheson Gas Data Book, Matheson Company Inc., Lyndhurst, New Jersey. (1980).

Braley, G.K., "Several Remedies for the Treatment of Spillages of Liquid Hazardous Chemicals", Proceedings of the 1980 National Conference on Control of Hazardous Material Spills. (May, 1980).

Brenchley, D.L., Assessment of Research and Development Needs in Ammonia Safety and Environmental Control, Pacific Northwestern Laboratory, PNL-4006, UC-11. (1981).

Bretherick, L., Handbook of Reactive Chemical Hazards, Second Edition, Butterworths, London, England. (1979).

Brownell, C.L., "Water Quality Requirements for First Feeding in Marine Fish Larvae. 1. Ammonia, Nitrite, Nitrate", J. Exper. Mar. Biol. Ecol., Vol. 44, No. 2-3, pp. 269-284. (1980).

Buchan, Lawton, Parent Ltd., A Survey of Self-contained Breathing Apparatus and Totally-encapsulated Chemical Protection Suits, Unedited Version. Not dated.

Buckley, J.A., "Acute Toxicity of Un-ionized Ammonia to Fingerling Coho Salmon", Prog. Fish Cult., Vol. 40, pp. 30-32. (1978).

Canadian Chemical Producers' Association, Private Communication, Ottawa, Ontario. (1982).

Canadian Transport Commission, Regulations for the Transportation of Dangerous Commodities by Rail, published by Supply and Services Canada, Ottawa, Ontario. (1974).

Clayton, G.D., Clayton, F.E. (ed.), Patty's Industrial Hygiene and Toxicology, Vols. 2A, 2B, Third Revised Edition, John Wiley and Sons Canada Limited, Toronto, Ontario. (1981).

Colt, J., Tchobanoglous, G., "Evaluation of the Short-term Toxicity of Nitrogeneous Compounds to Channel Catfish, Ictalurus Punctatus", Aquaculture, Vol. 8, pp. 209-224. (1976).

Colt, J., Tchobanoglous, G., "Chronic Exposure of Channel Catfish, Ictalurus Punctatus, to Ammonia: Effects on Growth and Survival", Aquaculture, Vol. 15, pp. 353-372. (1978).

Compressed Gas Association Inc., Anhydrous Ammonia, New York, New York. (1970).

Compressed Gas Association, Inc., Handbook of Compressed Gases, Second Edition, Van Nostrand Reinhold Company, New York, New York. (1981).

Corpus Information Services Ltd., "Ammonia", Chemical Product Profiles, Don Mills, Ontario. (1983).

Cotton, F.A., Wilkinson, G., Advanced Inorganic Chemistry, Interscience Publishers, New York, New York. (1972).

M.M. Dillon, Survey of Countermeasures Systems for Hazardous Material Spills, Environment Canada, Ottawa, Canada. (1982).

DOM-X, DOM-X Plastic Pipe Engineering Data, Toronto, Ontario. (1967).

Dow Chemical Canada Inc., "Ammonia, Anhydrous Technical", Emergency Response Information Sheet, Sarnia, Ontario. (April, 1981).

Dow Chemical Company, Dow Chemical Resistance Guide for Dow Plastic Lined Piping Products, Midland, Michigan. (1972).

Dow Chemical Company, Dow Plastic Lined Piping Systems, Midland, Michigan. (1972).

Drake, E., et al., A Feasibility Study of Response Techniques for Discharges of Hazardous Chemicals that Disperse Through the Water Column, U.S. Coast Guard, Washington, D.C., CG-D-16-77. (July, 1976).

Dreisbach, R.H., Handbook of Poisoning: Prevention, Diagnosis, and Treatment, Tenth Edition, Lange Medical Publications, Los Altos, California. (1980).

Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratories, Cincinnati, Ohio. (1979).

Environmental Protection Agency, Treatability Manual, Volume V, Summary, U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., EPA 600/8-80-042E. (July, 1980).

Environmental Protection Agency, Supplement to Development Document: Hazardous Substances Regulations, Section 311 Federal Water Pollution Control Act, U.S. Environmental Protection Agency, Office of Water and Standards, Washington, D.C., EPA 440/9-75-009. (November, 1975).

Environmental Science and Technology. (1978).

Epifanio L.E., Srna, R.F., "Toxicity of Ammonia Nitrate Ion and Orthophosphate to Mercenaria Mercenaria and Crassostrea Virginica", Mar. Biol., Vol. 33, pp. 241-246. (1975).

Evans, J.W., The Construction and Use of a Continuous-flow Bioassay Apparatus to Determine a Preliminary Un-Ionized Ammonia 96-hour LC_{50} for the Crayfish (Orconectes Nais), Master's thesis, Kansas State University. (1979).

Erco Industries Limited, Hazards of Chemicals Manual, Islington, Ontario. (March, 1981).

General American Transportation Corporation, Tank Car Manual, Chicago, Illinois. (May, 1979).

General Electric Company, Material Safety Data Sheets, Material Safety Information Services, Schenectady, New York. (November, 1979).

GF Plastic Systems Inc., GF Plastic Systems, Santa Ana, California. Not dated.

Gilreath, E.S., Qualitative Analysis using Semimicro Methods, McGraw-Hill Book Company, New York, New York, p. 221. (1954).

Gosselin, R.E., Hodge, H.C., Smith, R.P., Gleason, M.N., Clinical Toxicology of Commercial Products, 4th Edition, The Williams & Wilkins Co. (1976).

Grayson, M., Eckroth, D. (ed.), Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, John Wiley & Sons Inc., New York, New York. (1978).

Grayson, M., Eckroth, D. (ed.), Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 2, John Wiley & Sons Inc., New York, New York. (1980).

GSR Fluid Handling, Thermoplastic Piping Systems, Sun Valley, California. (1978).

Gupta, K., Development of a Mobile Treatment System for Handling Spilled Hazardous Materials, U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, EPA 600/2-76-109. (July, 1976).

Hatayama, H.K., Chen, J.J., deVera, E.R., Stephens, R.D., Storm, D.L., A Method for Determining the Compatibility of Hazardous Wastes, U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Office of Research and Development, Cincinnati, Ohio. (April, 1980).

Hazel, C.R., Thomsen, W., Meith, S.J., "Sensitivity of Striped Bass and Stickleback to Ammonia in Relation to Temperature and Salinity", Calif. Fish Game, Vol. 57, pp. 138-153. (1971).

Hazel, R.H., Burkhead, C.E., Huggins, D.G., The Development of Water Quality Criteria for Ammonia and Total Residual Chlorine for the Protection of Aquatic Life in Two Johnson County, Kansas, Streams, U.S. Department of the Interior, Office of Water Research and Technology, Washington, D.C. (1979).

Heller, H., Aqueous Ammonia Liquid/Vapour Composition Nomograph, Chemical Engineering, McGraw-Hill Book Company, New York, New York, pp. 131-132. (December, 1978).

Herbert, D.W.M., Shurben, D.S., "The Toxicity to Fish of Mixtures of Poisons. I. Salts of Ammonia and Zinc", Ann. Appl. Biol., Vol. 53, pp. 33-41. (1964).

Herbert, D.W.M., Shurben, D.S., "The Susceptibility of Salmonid Fish to Poisons Under Estuarine Conditions. II. Ammonia Chloride", Int. J. Air Water Pollut., Vol. 9, pp. 89-91. (1965).

Hesse, P.R., A Textbook of Soil Chemical Analysis, Chemical Publishing Co. Inc., New York, New York, p. 168. (1972).

Huibregtse, K.R., et al., Manual for the Control of Hazardous Material Spills - Volume One - Spill Assessment and Water Treatment Techniques, U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, EPA 660/2-77-227. (November, 1977).

Hydraulic Institute, Hydraulic Institute Standards, 12th Edition, New York, New York. (1969).

International Labour Organization, Occupational Exposure Limits for Airborne Toxic Substances, Second (Revised) Edition, Geneva, Switzerland. (1980).

International Technical Information Institute, Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazard Data, Japan. (1981).

Jenkins Brothers, Jenkins Corrosion Resistant Stainless Steel Valves, New York, New York. (1979).

Jolly, W.L., The Inorganic Chemistry of Nitrogen, W.A. Benjamin, Inc., New York, New York. (1964).

Jude, D.J., Sublethal Effects of Ammonia and Cadmium on Growth of Green Sunfish, Ph.D. dissertation, Michigan State University. (1973).

Kane, L.E., Barrow, C.S., Alarie, Y., "A Short-term Test to Predict Acceptable Levels of Exposure to Airborne Sensory Irritants", American Industrial Hygiene Association Journal, Vol. 40, No. 3, p. 207. (1979).

Katz, M., Methods of Air Sampling and Analysis, Second Edition, American Public Health Association, Washington, D.C., Method 402. (1977).

Kormondy, E.J., Concepts of Ecology, Prentice-Hall Inc., Englewood Cliffs, New Jersey. (1969).

Lefèvre, M.J., Becker, E.O., First Aid Manual for Chemical Accidents - For Use with Nonpharmaceutical Chemicals, Dowden, Hutchinson, and Ross Inc., Stroudsburg, Pennsylvania. (1980).

Leonardos, G., Kendall, D., Bernard, N., "Odor Threshold Determinations of Odorant Chemicals", Journal of Air Pollution Control Association, Vol. 19, No. 2, p. 91. (1969).

Lewis, R.J., Tatken, R.L., Registry of Toxic Effects of Chemical Substances, 1979, Vols. 1 and 2, National Institute for Occupational Safety and Health (NIOSH), Cincinnati, Ohio. (September, 1980).

Manufacturing Chemists Association, Aqua Ammonia, Washington, D.C. (1947).

Manufacturing Chemists Association, Anhydrous Ammonia, Washington, D.C. (1960).

Matheson Company Inc., Matheson Gas Data Book, East Rutherford, New Jersey. (1966).

McKee, J.E., Wolf, H.W., Water Quality Criteria, Second Edition, Resources Agency of California, State Water Quality Control Board. (1963).

McNeily, R.N., Neimans, V.P., Dwyer, L., Water Quality Sourcebook: A Guide to Water Quality Parameters, Inland Waters Directorate, Water Quality Branch, Environment Canada, Ottawa, Canada. (1979).

"More Ammonia PE for CIL", Canadian Chemical Processing, Vol. 66, No. 2, p. 14. (March, 1982).

National Academy of Sciences, Water Quality Criteria 1972, A Report of the Committee on Water Quality Criteria, Environmental Studies Board, National Academy of Sciences, Washington, D.C., pp. 186-188, 242, 450-461. (1972).

National Association of Corrosion Engineers, Corrosion Data Survey, Houston, Texas. (1967).

National Fire Protection Association, Fire Protection Guide on Hazardous Materials, Seventh Edition, Boston, Massachusetts. (1978).

National Institute for Occupational Safety and Health, Registry of Toxic Effects of Chemical Substances, U.S. Department of Health and Human Services, Microfiche. (October, 1981).

National Institute for Occupational Safety and Health, Manual of Analytical Methods, Second Edition, Vol. 1, Cincinnati, Ohio. (April, 1977).

National Institute for Occupational Safety and Health, Criteria for a Recommended Standard - Occupational Exposure to Ammonia, U.S. Department of Health, Education and Welfare, Cincinnati, Ohio, NIOSH 74-136. (1974).

National Research Council (United States), Ammonia, Committee on Medical and Biological Effects of Environmental Pollutants, Division of Medical Sciences, Assembly of Life Sciences, University Park Press, Baltimore, Maryland. (1979).

National Safety Council, Anhydrous Ammonia, Data Sheet No. 1-251-79, Chicago, Illinois. (1979).

National Safety Council, Data Sheet for Anhydrous Ammonia, National Safety Council, Chicago, Illinois, 1-251-79. (Revised 1979).

Oceanology International. (October, 1970).

Oil and Hazardous Materials Technical Assistance Data System, U.S. Environmental Protection Agency, Oil and Special Materials Control Division, Office of Water Program Operations, Washington, D.C., Microfiche. (1977).

Oil and Hazardous Materials Technical Assistance Data System, U.S. Environmental Protection Agency, Oil and Special Materials Control Division, Office of Water Program Operations, Washington, D.C. (1981).

Oil and Hazardous Materials - Emergency Procedures in the Water Environment, U.S. Department of Interior, Edison, New Jersey. (October, 1968).

Ontario Ministry of the Environment, Water Management Goals, Policies, Objectives and Implementation Procedures for the Ministry of the Environment, Toronto, Ontario. (November, 1978).

Ontario Ministry of the Environment, "The Environmental Protection Act, Statutes of Ontario 1971", Chapter 86, as amended; and Regulation 15 (General) as amended. (1971).

Ontario Ministry of the Environment, Personal Communication, Sarnia, Ontario. (19 January 1982).

Orion Research Technical Literature, Method 502, Cambridge, Massachusetts. Not dated.

Perry, R.H., Chilton, C.H. (ed.), Chemical Engineer's Handbook, Fifth Edition, McGraw-Hill Book Company, New York, New York. (1973).

Peterson, S.E., Schutsky, R.M., Rosage, T.F., Supplementary Material on Toxicity of Ammonia to Selected Fishes of the Conestoga River, Lancaster County, Ichthyological Associates, Inc., Unpublished. (1977).

Pierce, W.C., Sawyer, D.T., Haenisch, E.L., Quantitative Analysis, 4th Edition, John Wiley & Sons, New York. (1958).

Pilie, R.J., et al., Methods to Treat, Control and Monitor Spilled Hazardous Materials, U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, EPA 670/2-75-042. (June, 1975).

Proctor, N.H., Hughes, J.P., Chemical Hazards of the Workplace, J.B. Lippincott Company, Toronto, Ontario. (1978).

Raj, P.P.K., Lakekar, A.S., Assessment Models in Support of Hazard Assessment Handbook, Prepared for the Department of Transportation, U.S. Coast Guard, Washington, D.C., p. 238. (January, 1974).

Raj, P.P.K., Reid, R.C., "Fate of Liquid Ammonia Spilled onto Water", Environmental Science and Technology, Vol. 12, No. 13, pp. 1422-1425, American Chemical Society, Washington, D.C. (December, 1978).

Reddy, N.A., Menon, N.R., "Effects of Ammonia and Ammonium on Tolerance and Byssogenesis in Perna Viridis", Marine Ecology - Progress Series, Vol. 1, No. 4, pp. 315-322. (1979).

Rehau, Mechan-O-Joint Water Pressure Pipe and Fittings, Montreal, Quebec. (1978).

Resplandy, A., "Etude expérimentale des propriétés de l'ammonia conditionnant les mesures à prendre pour la sécurité du voisinage des stockages industriels Chemi et Industrie", Genie Chimique, Vol. 102, pp. 691-702. (1969).

Robinette, H.R., "Effect of Selected Sublethal Levels of Ammonia on the Growth of Channel Catfish (Ictalurus Punctatus)", Prog. Fish. Cult., Vol. 38, pp. 26-29. (1976).

Robbins, T.W., Peterson, S.E., Schutsky, R.M., Rosage, T.F., Toxicity of Ammonia to Selected Fishes of the Conestoga River, Lancaster County, Ichthyological Associates, Inc., Unpublished. (1977).

Robinson-Wilson, E.F., Seim, W.K., "The Lethal and Sublethal Effects of a Zirconium Process Effluent on Juvenile Salmonids", Water Resour. Bull., Vol. 11, No. 5, pp. 975-986. (1975).

Rosage, T.F., Schutsky, R.M., Rapp, K.M., "Toxicity of Un-Ionized Ammonia to the Spotfin Shiner (Notropis Spilopterus)", Proc. Pa. Acad. Sci., Vol. 53, pp. 39-42. (1979).

Roseboom, D.P., Richey, D.L., Acute Toxicity of Residual Chlorine and Ammonia to Some Native Illinois Fishes, Illinois State Water Survey, Illinois, ISWS/RI-85/77. (1977).

Rosenstock, H.M., Draxl, K., Steiner, B., Herron, J.T., Energetics of Gaseous Ions, National Bureau of Standards, Washington, D.C. (1977).

Rubin, A.J., Elmaraghy, G.A., "Studies on the Toxicity of Ammonia, Nitrate and their Mixtures to Guppy Fry", Water Res., Vol. 11, pp. 927-935. (1977).

Sax, N.I., Dangerous Properties of Industrial Materials, Fifth Edition, Van Nostrand Reinhold Company, New York, New York. (1979).

Scarterfield, J., Ministry Investigation of Tanker Truck Accident Involving the Escape of Anhydrous Ammonia Vapour, June 15, 1981, Ministry of the Environment, Industrial Abatement Section, Sarnia, Ontario. (1981).

Scott's Industrial Directory of Ontario Manufacturers, 12th Edition, Penstock Directories Limited, Oakville, Ontario. (1979).

Shreve, R.N., Brink, J.A., Chemical Process Industries, Fourth Edition, McGraw-Hill Book Company, New York, New York. (1977).

Sisler, H.H., Chemistry in Non-aqueous Solvents, Reinbold Publishing Corp., New York, New York. (1961).

Smart, G., "Investigations of the Toxic Mechanism of Ammonia to Fish: Gas Exchange in Rainbow Trout (Salmo Gairdneri) Exposed to Acutely Lethal Concentrations", Journal of Fish Biology, Vol. 12, pp. 93-104. (1978).

Southam Business Publications Ltd., "1981 Chemical Buyers' Guide", Canadian Chemical Processing, Vol. 64, No. 9, Don Mills, Ontario. (December, 1980).

Spehar, R.L., Lemke, A.E., et al., "Effects of Pollution on Freshwater Fish", Journal of Water Pollution Control Federation, Vol. 53, No. 6, pp. 1028-1076. (June, 1981).

Stevenson, T.J., The Effect of Ammonia, pH and Salinity on the White Perch Morone Americana, Ph.D. dissertation, University of Rhode Island. (1977).

Stull, D.R., Prophet, H., JANAF Thermochemical Tables, Second Edition, U.S. National Bureau of Standards, Office of Standard Reference Data, Washington, D.C. (June, 1971).

Sullivan, R.J., Air Pollution Aspects of Odorous Compounds, U.S. Department of Commerce, PB 188089. (1969).

Thurston, R.V., Russo, R.C., "Ammonia Toxicity to Fishes. Effect of pH on the Toxicity of the Un-ionized Ammonia Species", Environmental Science and Technology, Vol. 15, No. 7, pp. 838-840. (July, 1981).

Thurston, R.V., Russo, R.C., Smith, C.E., "Acute Toxicity of Ammonia and Nitrate to Cutthroat Trout Fry", Transactions of the American Fisheries Society, Vol. 107, No. 2, pp. 361-368. (1978).

Todd, D.K., The Water Encyclopedia, Maple Press, New York, New York. (1970).

Tommasso, J.R., Goudie, G.A., Sumco, B.A., Davis, K.B., "Effects of Environmental pH and Calcium on Ammonia Toxicity in Channel Catfish", Trans. Am. Fish. Soc., Vol. 109, pp. 229-234. (1980).

Toxicology Testing in Progress, Sponsored by Toxicology Information Subcommittee, DHEW Committee to Coordinate Environmental and Related Programs, Available from the National Library of Medicine and NTIS. (1981).

Transport Canada, Transportation of Dangerous Goods Code, Vol. 1 (Lists), Vol. 2, Ottawa, Ontario. (June, 1980).

Union Carbide Canada Limited, Linde Specialty Gases, Oakville, Ontario. (1981).

Uniroyal, Guide to Polymer Properties, Uniroyal Inc., Mishawaka, Indiana. Not dated.

U.S. Department of Health, Education, and Welfare, Air Pollution Abatement Manual, Cincinnati, Ohio. (1967).

U.S. Department of Health, Education and Welfare, Pocket Guide to Chemical Hazards, U.S. Department of Health, Education and Welfare, and U.S. Department of Labor, Washington, D.C. (1978).

U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health (NIOSH), U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), Occupational Health Guidelines for Chemical Hazards, NIOSH Publication No. 81-123. (1981).

U.S. Department of Transportation, Emergency Action Guide for Selected Hazardous Materials, Research and Special Programs Administration, Materials Transportation Bureau, Washington, D.C. (1978).

U.S. Department of Transportation, Hazardous Materials, 1980 Emergency Response Guidebook, Research and Special Programs Administration, Materials Transportation Bureau, Washington, D.C. (1980).

U.S. Department of Transportation, Coast Guard, CHRIS Hazard Assessment Handbook, Washington, D.C., CG-446-3. (April, 1974).

U.S. Department of Transportation, Coast Guard, Chemical Hazards Response Information System (CHRIS), Washington, D.C. (1978).

Verschueren, K., Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Company, New York, New York. (1977).

Vrolyk, J.J., et al., Prototype System for Plugging Leaks in Ruptured Containers, U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, EPA 600/2-76-300. (December, 1976).

"Water Quality Criteria for European Freshwater Fish", Water Research, Vol. 7, pp. 1011-1022. (1973).

Weast, R.C. (ed.), CRC Handbook of Chemistry and Physics, 60th Edition, Chemical Rubber Publishing Company, Cleveland, Ohio. (1982).

Wickens, J.F., "The Tolerance of Warmwater Prawns to Recirculated Water", Aquaculture, Vol. 9, pp. 19-37. (1976).

Yaws, C.L., "Physical and Thermodynamic Properties", Chemical Engineering, Vol. 81, No. 25, p. 91. (25 November 1974).

Yopp, J.H., Schmid, W.E., Holst, R.W., Determination of Maximum Permissible Levels of Selected Chemicals that Exert Toxic Effects on Plants of Economic Importance in Illinois, NTIS, Springfield, Virginia, PB-327-654. (August, 1974).

EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc.	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immision concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)

MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
T_d	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
T_s	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight