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ENVIRO

Technical

Information for

Problem

Spills

MORPHOLINE

TP
248
.E72
M8313
1985

February 1985

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.

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MORPHOLINE

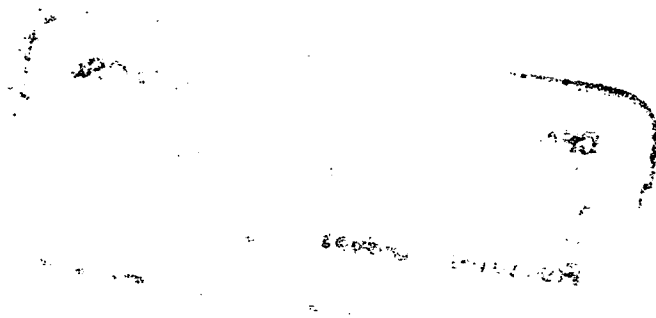
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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS



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

February 1985



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 wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

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. 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.

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1 SUMMARY

MORPHOLINE (C₄H₉ONH)

Colourless, oily liquid with a fishy, ammonia-like odour

SYNONYMS

Diethyleneimide Oxide; Diethylene Imidoxide; Diethylene Oximide; Diethylenimide Oxide; p-Isloxazine, Tetrahydro-; 1-Oxa-4-Azacyclohexane; 2H-1,4-Oxazine, Tetrahydro-; 4H-1,4-Oxazine, Tetrahydro; Tetrahydro-1,4-Isloxazine; Tetrahydro-1,4-Oxazine; Tetrahydro-2H-1,4-Oxazine

IDENTIFICATION NUMBERS

UN No. 2054; CAS No. 110-91-8; OHM-TADS No. 7216806; STCC No. 4907864, 4935668 or 4907397

GRADES & PURITIES

Technical, 99 percent and greater

IMMEDIATE CONCERNS

Fire: Flammable. Flashback along vapour trail may occur

Human Health: Highly toxic by skin absorption and moderately toxic by inhalation

Environment: Harmful to aquatic life

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): liquid

Boiling Point: 128.9°C

Melting Point: -4.9°C

Flammability: flammable

Flash Point: 35°C (CC)

Vapour Pressure: 0.93 kPa (20°C)

Density: 1.0005 g/cm³ (20°C)

Solubility (in water): soluble in all proportions

Behaviour (in water): neutrally buoyant depending on conditions; mixes rapidly

Behaviour (in air): vapour is heavier than air

Odour Threshold: 0.01 to 0.14 ppm

ENVIRONMENTAL CONCERNS

Morpholine is harmful to aquatic life at levels as low as 100 mg/L. It degrades at a moderate rate.

HUMAN HEALTH

TLV®: 20 ppm (70 mg/m³) (skin)

IDLH: 8000 ppm

Exposure Effects

- Inhalation:** Irritation to respiratory tract, possibly coughing, nausea, headache and difficult breathing.
- Contact:** Skin contact will cause irritation and burns. Absorption will cause headache and nausea. Contact with the eyes will cause temporary fogging of vision, irritation, burns and possible corneal edema.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "FLAMMABLE". Call fire department and notify distributor. Eliminate sources of ignition including traffic and equipment. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Use alcohol foam, dry chemical, carbon dioxide, water spray or fog to extinguish. Cool fire-exposed containers with water. Containers may explode in heat of fire. Stay clear of tank ends.

COUNTERMEASURES

Emergency Control Procedures in/on

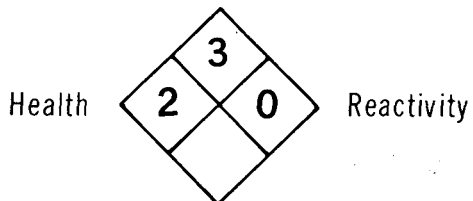
- Soil:** Construct barriers to contain spill or divert to impermeable holding area. Remove material with pumps or vacuum equipment. Absorb residual liquid with natural or synthetic sorbents.
- Water:** Contain contaminated water by damming, water diversion or natural barriers. Use sodium dihydrogen phosphate to neutralize contaminated water.
- Air:** Use water spray to knock down vapour. Control runoff for later treatment and/or disposal.

NAS HAZARD RATING

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

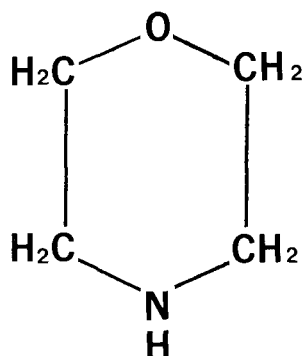
**NFPA
HAZARD
CLASSIFICATION**

Flammability



2 PHYSICAL AND CHEMICAL DATA

Chemical Structure



Physical State Properties

Appearance	Colourless liquid (Verschueren 1984)
Usual shipping state	Liquid (Verschueren 1984)
Physical state at 15°C, 1 atm	Liquid
Freezing point	-4.9°C (Kirk-Othmer 1978)
Boiling point	128.9°C (Kirk-Othmer 1978)
Vapour pressure	0.93 kPa (20°C) (Union Chem. 1976)

Densities

Density	1.0005 g/cm ³ (20°C) (PPCC 1955) 0.994 g/cm ³ (25°C) (PPCC 1955)
Specific gravity, liquid (water=1)	1.002 (20°/20°C) (Union Chem. 1976), 1.00 (20°/4°C) (Verschueren 1984)
Specific gravity, vapour (air=1)	3.0 (Ashland MSDS 1978)

Fire Properties

Flammability	Flammable liquid (NFPA 1978)
Flash point	
CC	35°C (Kirk-Othmer 1978)
OC	38°C (NFPA 1978)
Autoignition temperature	310°C (NFPA 1978), 275°C (Ullmann 1975)
Burning rate	1.9 mm/min (CHRIS 1978)
Upper flammability limit	11.2 percent (v/v) (NFPA 1978), 15.2 percent (v/v) (Ullmann 1975)
Lower flammability limit	2.0 percent (v/v) (NFPA 1978), 1.8 percent (v/v) (Ullmann 1975)

Flashback potential	Vapour may travel considerable distance to a source of ignition and flash back (NFPA 1978)
Electrical ignition hazard	May be ignited by static discharge
Other Properties	
Molecular weight of pure substance	87.12 (CRC 1980)
Constituent components of typical commercial grade	99.0 percent (min) morpholine, 0.5 percent (max) water (Ashland TD 1980)
Refractive index	1.4548 (20°C) (CRC 1980)
Viscosity	2.23 mPa·s (20°C) (Merck 1976), 1.52 mPa·s (40°C) (PPCC 1955)
Liquid interfacial tension with air	37.5 mN/m (20°C) (Kirk-Othmer 1978)
Hygroscopicity	Hygroscopic (NFPA 1978)
Latent heat of sublimation	43.96 kJ/mole (25°C) (Kirk-Othmer 1978)
Latent heat of vaporization	37.03 kJ/mole (128.3°C) (Kirk-Othmer 1978)
Heat of formation	-154.8 kJ/mole (20°C) (Benson 1958)
pH of solutions	13 (pure liquid), 12 (26 percent solution) (ISH 1977)
Heat capacity	
Constant pressure (C_p)	174 J/(mole·°C) (25°C) (Kirk-Othmer 1978)
Critical pressure	5302 kPa (Ullmann 1975)
Critical temperature	344°C (Ullmann 1975)
Log ₁₀ octanol/water partition coefficient	-1.08 (Hansch and Leo 1979)
Dielectric constant	7.18 (Kirk-Othmer 1978)
Dipole moment	1.58 D (Kirk-Othmer 1978)
Conductivity (electrical)	6.0×10^{10} ohm ⁻¹ cm ⁻¹ (Kirk-Othmer 1978)
Evaporation rate	0.27 g/(m ² s) (20°C, wind 4.5 m/s) (this work)
Solubility	
In water	Soluble in all proportions (Union Chem. 1976)
In other common materials	Infinitely soluble in acetone, benzene, butyl ether, ethanol, ethylene glycol, ethyl ether and methanol. Soluble in methyl amine (33 g/100 mL) and dimethylamine (109 g/100 mL) (ISH 1977)

Azeotropes

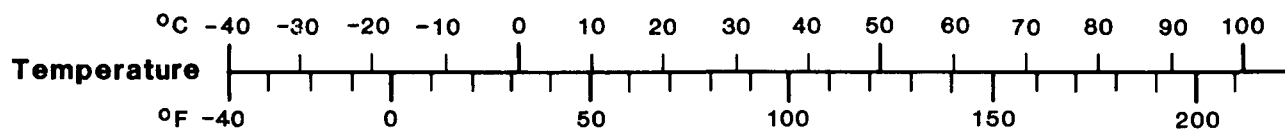
Forms azeotropes with 12 percent water, 88 percent morpholine, with freezing point below -50°C (Ullmann 1975)

**Vapour Weight to Volume
Conversion Factor**

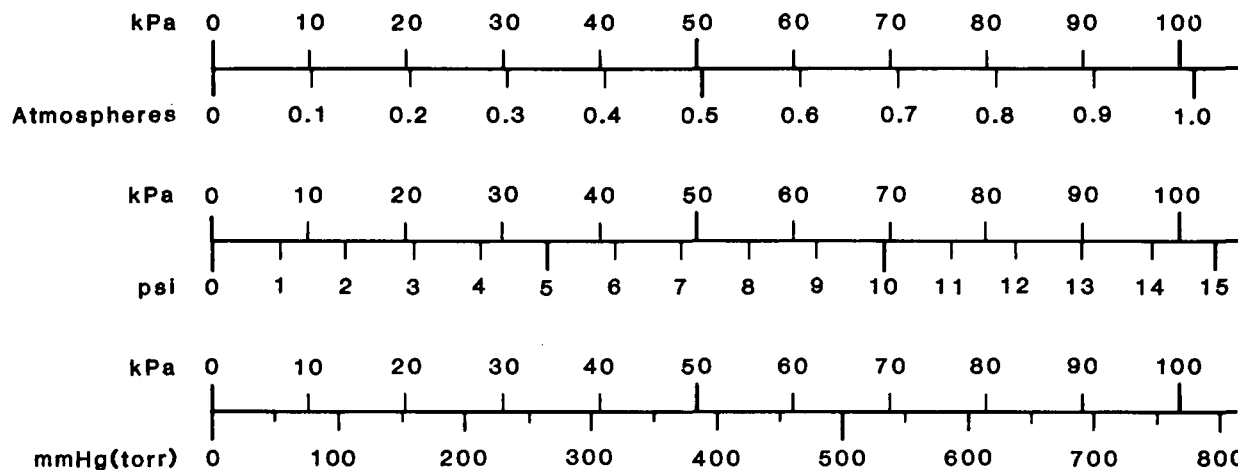
1 ppm = 3.617 mg/m^3
(Verschuereen 1984)

MORPHOLINE

CONVERSION NOMOGRAMS

**Pressure**

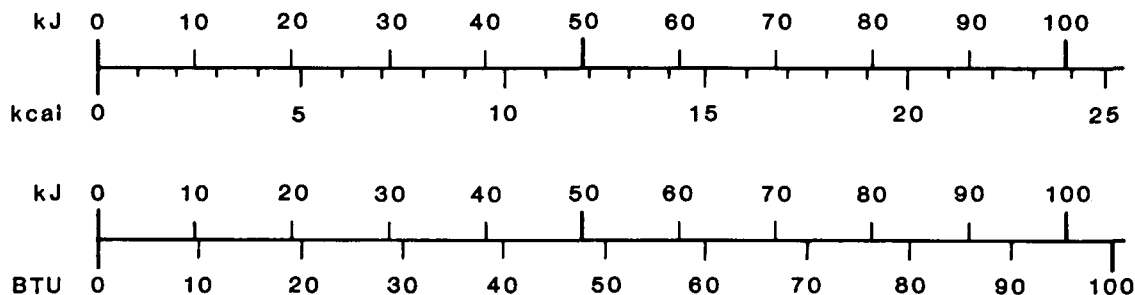
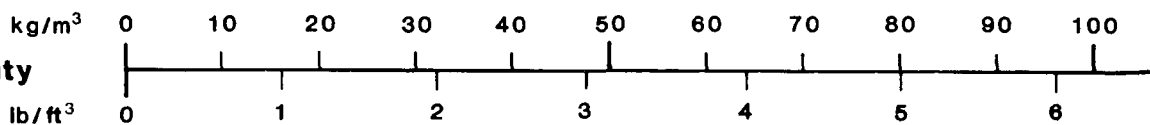
1 kPa = 1 000 Pa

**Viscosity**

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

Kinematic 1 m²/s = 1 000 000 centistokes (cSt)**Concentration (in water)**1 ppm \cong 1 mg/L**Energy (heat)**

1 kJ = 1 000 J

**Density**

MORPHOLINE

VAPOUR PRESSURE VS TEMPERATURE

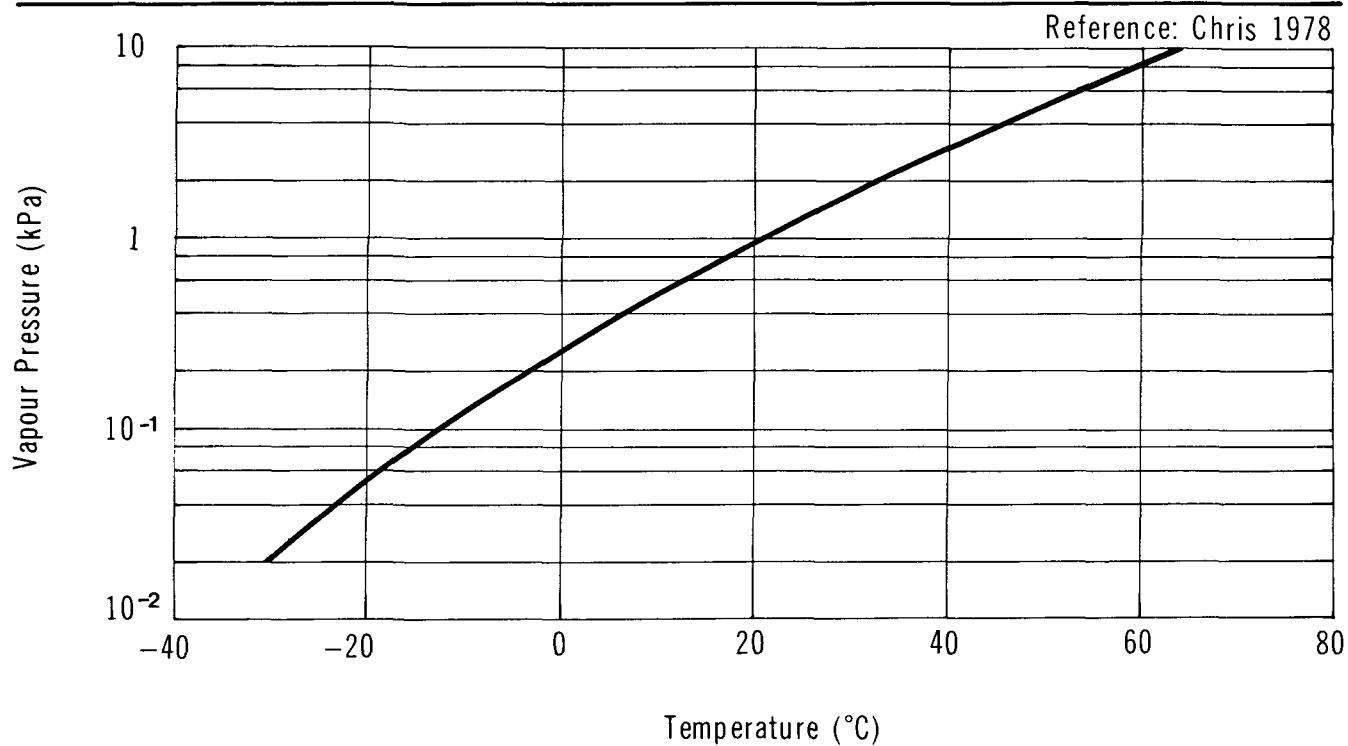
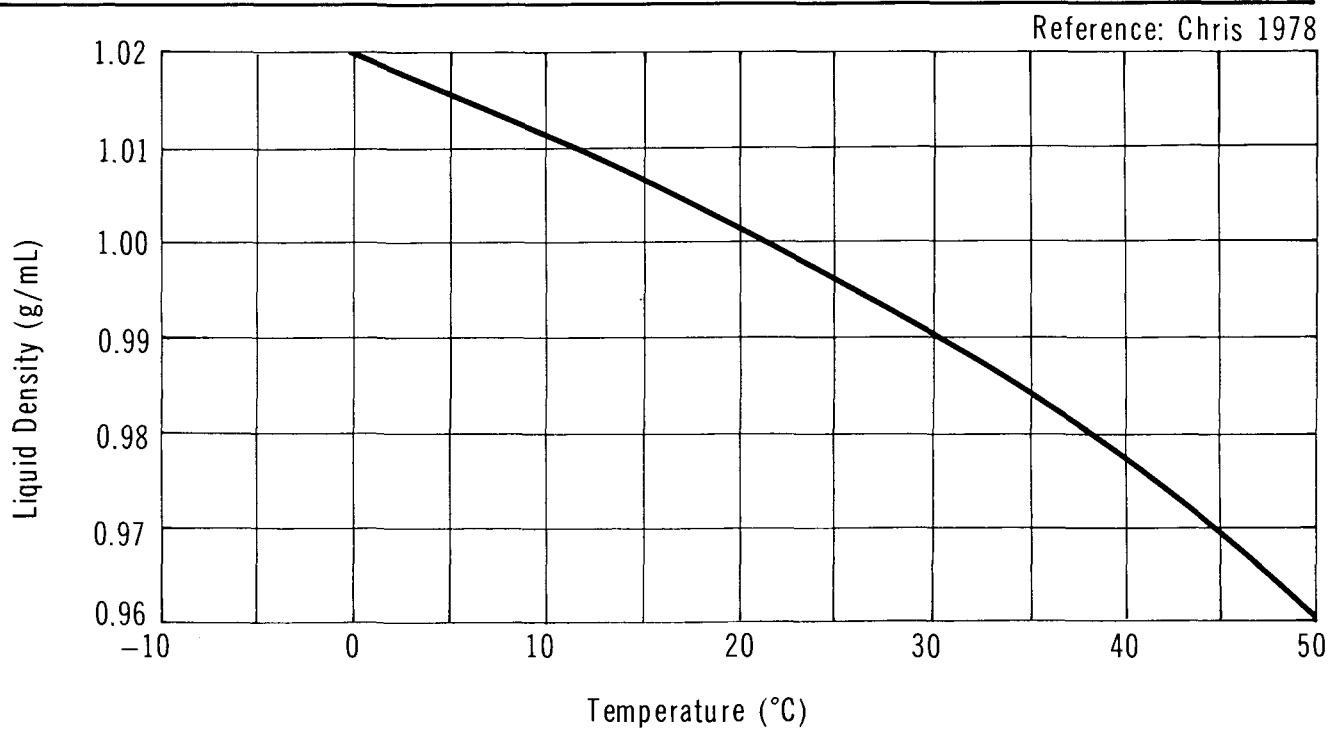


FIGURE 2

MORPHOLINE

LIQUID DENSITY VS TEMPERATURE



MORPHOLINE (Aqueous Solution)

VISCOSITY OF SOLUTIONS

Reference: ISH 1977

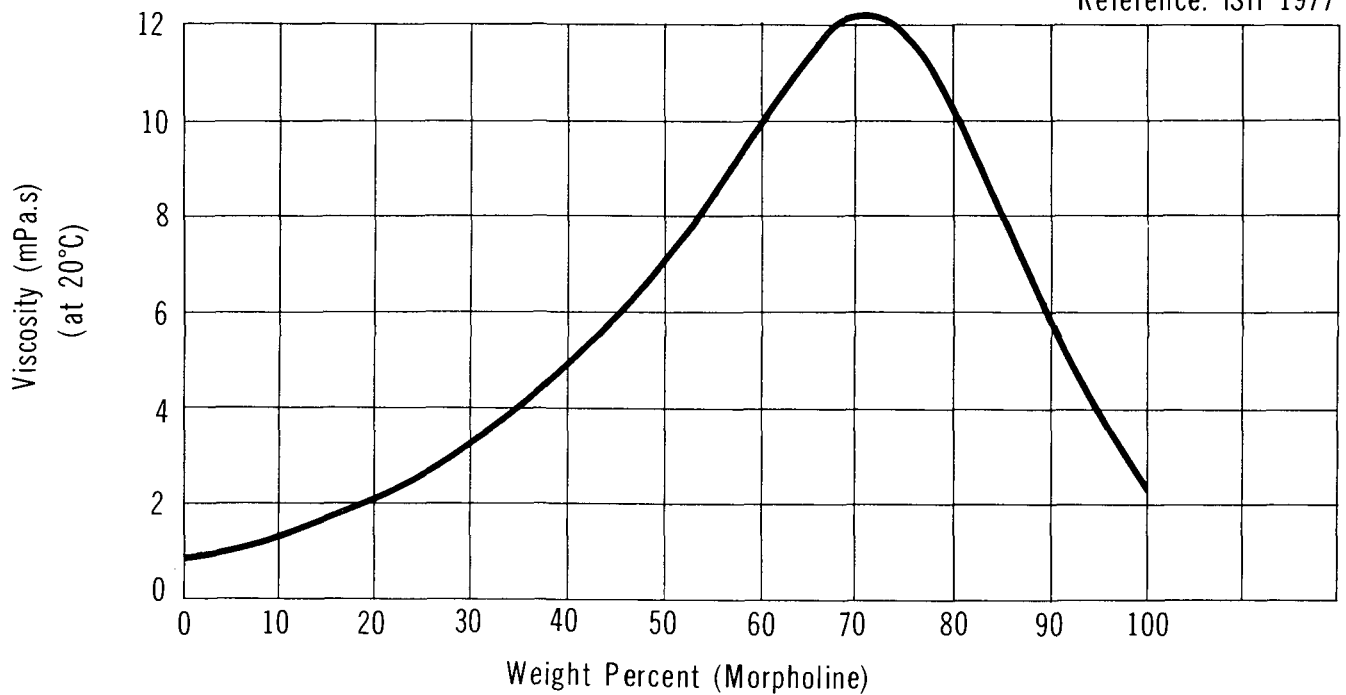
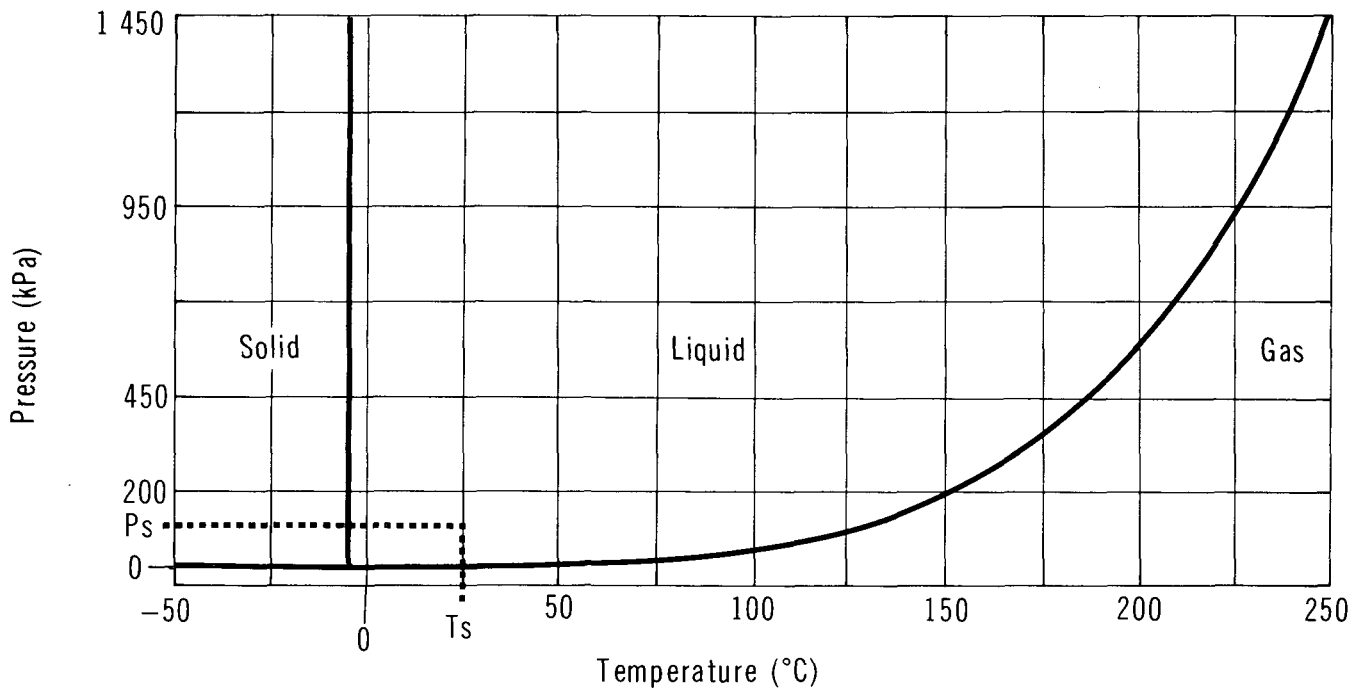


FIGURE 4

MORPHOLINE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Ashland MSDS 1978; Corpus 1979)

Morpholine is available in a technical grade with a minimum purity of 99 percent.

3.2 Domestic Manufacturers (Corpus 1979)

Morpholine is not produced in Canada. It is imported from the United States, United Kingdom and West Germany.

3.3 Suppliers (CBG 1980; CCPA 1981)

Morpholine is imported by the following Canadian distributors:

A & K Petro-Chem Industries Ltd.
710 Arrow Road
Weston, Ontario
M9M 2M1
(416) 746-2991

Canada Colours and Chemicals Ltd.
80 Scarsdale Road
Don Mills, Ontario
M3B 2R7
(416) 924-6831

Arliss Chemical Co. Inc.
325 Hymus Blvd.
Pointe Claire, Quebec
H9R 1G8
(514) 694-2170

Canadian Industries Ltd. (C-I-L)
General Chemicals Division
90 Sheppard Avenue East
Willowdale, Ontario
M2N 6H2
(416) 226-6110

Ashland Chemical/Solvents Division
Valvoline Oil/and Chem.
150 Bronoco Avenue
Toronto, Ontario
M6E 4Y1
(416) 651-2822

Ciscochem Inc.
63 Selby Road
Brampton, Ontario
L6W 1K5
(416) 459-4540

BASF Canada Ltd.
5850 Cote de Liesse
Montreal, Quebec
H4T 1C1
(514) 341-5411

Cote Chemicals Inc.
111 Bombardier Park
Chateauguay Centre, Quebec
J6J 3X0
(514) 691-6260

Bate Chemical Co. Ltd.
160 Lesmill Road
Don Mills, Ontario
M3B 2T7
(416) 445-7050

Harrisons & Crosfield (Canada) Ltd.
4 Banigan Drive
Toronto, Ontario
M4H 1G1
(416) 425-6500

International Chemical Canada Ltd.
P.O. Box 385
Brampton, Ontario
L6V 2L3
(416) 453-4234

Ternachem Inc.
310 Victoria Avenue, Suite 101
Montreal, Quebec
H3Z 2M9
(514) 487-2227

Kingsley & Keith (Canada) Ltd.
310 Victoria Avenue
Montreal, Quebec
H3Z 2M8
(514) 487-1550

Texaco Chemicals Canada Ltd.
250 Lakeshore Road West
Mississauga, Ontario
L5G 4M6
(416) 271-1702

Stanchem Div PPG Ind. Canada Ltd.
5029 St. Ambroise Street
Montreal, Quebec
H4C 2E9
(514) 933-6721

3.4 Major Transportation Routes

Morpholine is distributed mainly in drums from Montreal, Quebec, and Toronto, Ontario, to facilities in Ontario and Quebec.

3.5 Production Levels (Corpus 1979)

No Canadian plants currently produce morpholine.

Domestic Shipments (1977)	Nil
Imports (1977) (kilotonnes/year)	<u>399</u>
Total	<u>399</u>

3.6 Major Uses in Canada (Corpus 1979)

Morpholine is used as a neutralizing amine for water treatment, as a corrosion inhibitor, as an intermediate in rubber chemicals, and in the production of industrial floor polishes, waxes and washing powders, and pharmaceuticals.

3.7 Major Buyers in Canada (Corpus 1979)

Alchem, Burlington, Ont.
Betz Laboratories, Kanata, Ont.
Calgon Canada, Bramalea, Ont.
Dearborn Chemical, Mississauga, Ont.
Drew Chemical, Ajax, Ont.
McArthur Chemical, Montreal, Que.
Ontario Hydro, Toronto, Ont.
Perolin-Bird Archer, Cobourg, Ont.
Quadra Chemicals, Montreal, Que.
Quatic Chemicals, Guelph, Ont.
Uniroyal, Elmira, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Bulk transport of morpholine does not occur frequently. Transport is primarily in drums. Transportation vessels and containers under this category have been grouped under the classifications of railway tank cars and highway tank vehicles.

4.1.1.1 Railway tank cars. Railway tank cars used to transport morpholine are described in Table 2 (RTDCR 1974). Figure 5 shows a railway car used to transport morpholine; Table 3 indicates railway tank car details associated with this drawing. Cars are equipped for unloading by pump or gravity flow through a bottom outlet. The bottom outlet may be furnished with a steam jacket for cold weather off-loading. In addition to bottom unloading, the cars may be unloaded from the top by pump. In this case, the morpholine is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with an unloading connection valve. Air pressure is never used for unloading morpholine tanks (TCM 1979).

4.1.1.2 Tank motor vehicles. Morpholine is transported by tank motor vehicles with tanks classed as nonpressure vessels (TDGC 1980). Design pressure for such tanks does not exceed 21 kPa (3 psi). Motor vehicle tanks carrying morpholine are similar to the railway tanks previously described. These highway tankers are usually unloaded by pump from the top unloading connection valve. The off-loading equipment and procedures for tank motor vehicles are similar to those for railway tank cars, to be discussed later.

4.1.2 Packaging. Morpholine is primarily transported in drums. Drums fabricated from a variety of construction materials are permitted (TDGC 1980). Table 4 describes these drums.

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars.

Prior to off-loading, certain precautions must be taken (PC 1982):

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution signs displayed.

TABLE 2

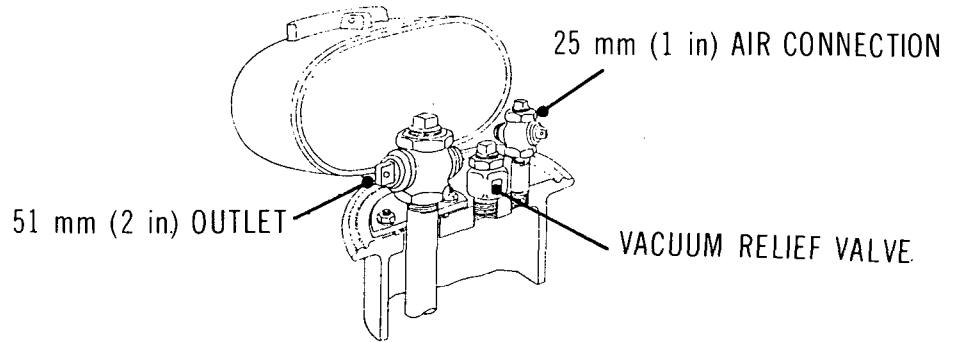
RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT Specification	Tank Material	Insulation	Test Pressure kPa (psi)	Dome	Bottom Outlet	Bottom Washout	Gauging Device
103W	Steel	optional	414 (60)	required	optional	optional	optional
103ALW	aluminum alloy	optional	414 (60)	required	optional	optional	optional
104W	steel	optional	414 (60)	required	optional	optional	optional
105A100W	steel	required	690 (100)	none	prohibited	prohibited	standard
105A100ALW	aluminum alloy	required	690 (100)	none	prohibited	prohibited	standard
109A100ALW	aluminum alloy	optional	690 (100)	none	prohibited	optional	standard
111A60W1	steel	optional	414 (60)	none	optional	optional	required
111A60ALW1	aluminum alloy	optional	414 (60)	none	optional	optional	required
111A60F1	steel	optional	414 (60)	none	optional	optional	required
111A100W3	steel	required	690 (100)	none	optional	optional	required
111A100W4	steel	required	690 (100)	none	prohibited	prohibited	required
111A100W6	alloy steel	optional	690 (100)	none	optional	optional	required
112A200W	steel	none	1380 (200)	none	prohibited	prohibited	standard
112A400F	steel	none	2760 (400)	none	prohibited	prohibited	standard
114A340W	steel	none	2340 (340)	none	optional	optional	standard

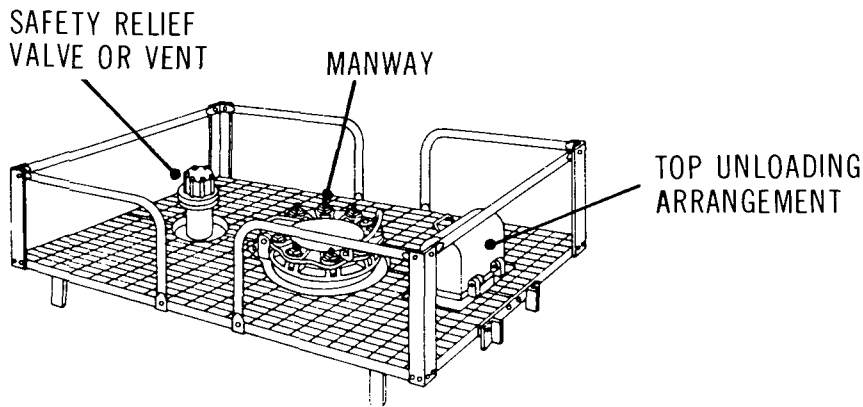
MORPHOLINE

RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979, RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

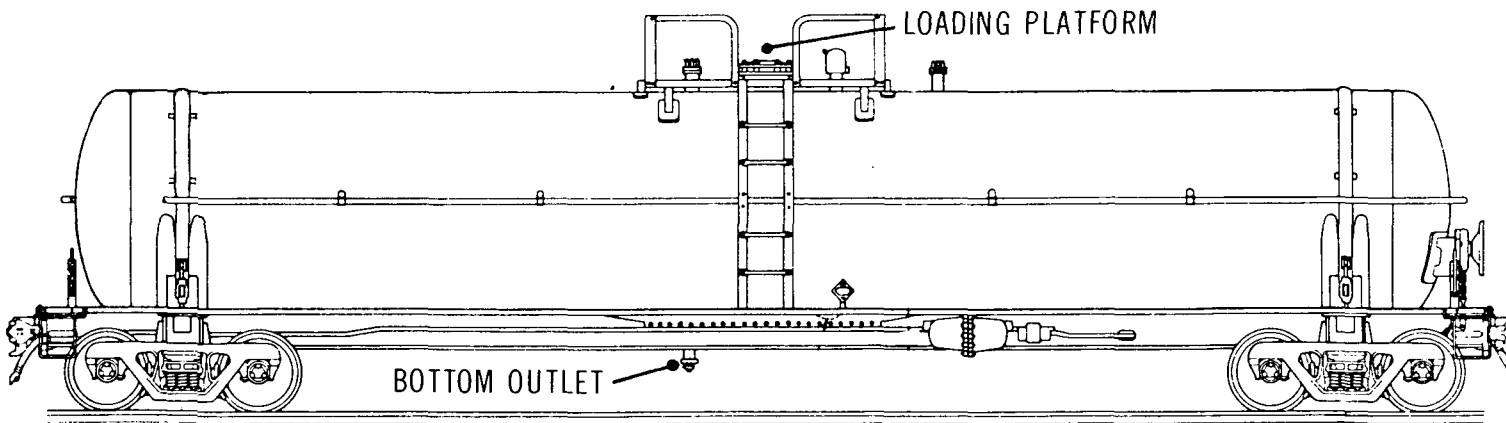


Illustration of tank car layout

TABLE 3

TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A60W1 (TCM 1979; RTDCR 1974)

Description	Tank Car Size (Imp. Gal.)					
	16 700		17 200		20 000	
<u>Overall</u>						
Nominal capacity	75 700 L	(16 700 gal.)	78 000 L	(17 200 gal.)	90 900 L	(20 000 gal.)
Car weight - empty	33 900 kg	(74 700 lb.)	33 900 kg	(74 700 lb.)	38 900 kg	(85 800 lb.)
Car weight - (max.)	119 000 kg	(263 000 lb.)	83 500 kg	(184 000 lb.)	119 000 kg	(263 000 lb.)
<u>Tank</u>						
Material	Steel		Steel		Steel	
Thickness	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)
Inside diameter	2.60 m	(102 in.)	2.62 m	(103 in.)	2.74	(108 in.)
Test pressure	414 kPa	(60 psi)	414 kPa	(60 psi)	414 kPa	(60 psi)
Burst pressure	1640 kPa	(240 psi)	1640 kPa	(240 psi)	1640 kPa	(240 psi)
<u>Approximate Dimensions</u>						
Coupled length	17 m	(57 ft.)	17 m	(57 ft.)	18 m	(60 ft.)
Length over strikers	16 m	(53 ft.)	16 m	(53 ft.)	17 m	(57 ft.)
Length of truck centres	13 m	(42 ft.)	13 m	(42 ft.)	14 m	(45 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)	4 m	(13 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)	5 m	(15 ft.)
Overall width (over grabs)	3.2 m	(127 in.)	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2-3 m	(8-10 ft.)	2-3 m	(8-10 ft.)	2-3 m	(8-10 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.)
<u>Loading/Unloading Fixtures</u>						
<u>Top Unloading</u>						
Unloading connection	51 mm	(2 in.)	51 mm	(2 in.)	51 mm	(2 in.)
Manway/fill hole	203-356 mm	(8-14 in.)	203-356 mm	(8-14 in.)	203-356 mm	(8-14 in.)
Air connection	25-51 mm	(1-2 in.)	25-51 mm	(1-2 in.)	25-51 mm	(1-2 in.)
<u>Bottom Unloading</u>						
Bottom outlet	102-152 mm	(4-6 in.)	102-152 mm	(4-6 in.)	102-152 mm	(4-6 in.)
<u>Safety Devices</u>						
	Safety vent or valve		Safety vent or valve		Safety vent or valve	
<u>Dome</u>						
	None		None		None	
<u>Insulation</u>						
	Optional		Optional		Optional	

TABLE 4 DRUMS

Type of Drum	Designation	Description	Figure No. (If any)
Steel	IA1	Nonremovable head, reusable	6
	IA1A	IA1 with reinforced chime	6
	IA1B	IA1 with welded closure flange	6
	IA1D	IA1 with coating (other than lead)	6
	IA2	Removable head, reusable	6
	IA3	Nonremovable head, single use only	6
Aluminum	IB1	Nonremovable head	6
	IB2	Removable head	6
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.)	
Fibreboard Drums with inner plastic receptacles	6HG1	Outer containers of convolutely wound plies of fibreboard. Inner plastic in shape of drum. Maximum capacity of 225 L (49 gal.)	

- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- Effectively ground the tank car.

Two means of off-loading are used for rail cars, top off-loading and bottom off-loading.

Proceed with top off-loading as follows (PC 1982):

- Relieve the tank of internal vapour pressure by cooling the tank with water or venting at short intervals.
- After removing the protective housing from the discharge line at the top of the car, connect the 51 mm (2 in.) unloading line.
- Off-load the tanker by pump only.

TYPICAL DRUM CONTAINERS

Typical steel drum

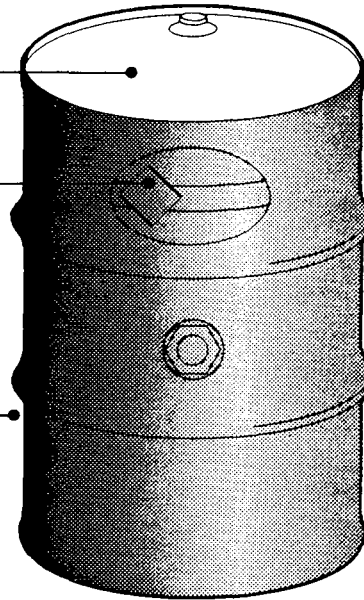
MIN. 2.4mm
LEAD COATING FOR
IAIC DESIGNATION

CONTENTS LABEL

BODY AND HEADS
CONSTRUCTED OF
ROLLED STEEL

MAX. CAPACITY
250 L

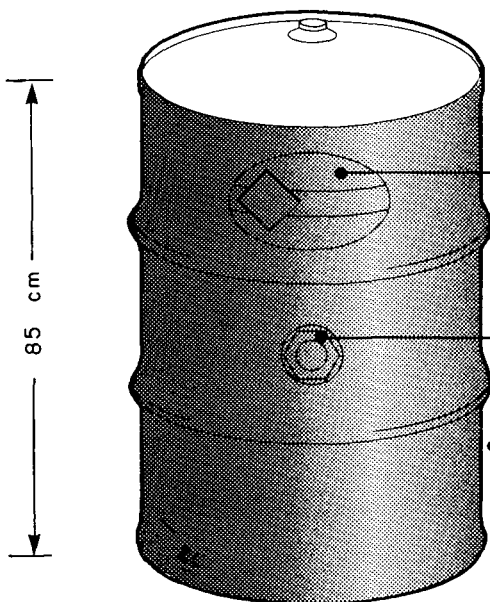
MAX. NET MASS
400 kg



85 cm

53 cm

Typical aluminum drum



85 cm

CONTENTS LABEL

MAX. DIAMETER
OPENING 70 mm

BODY AND HEADS
CONSTRUCTED OF
MIN. 99% PURE
ALUMINUM

MAX. CAPACITY
250 L
MAX. NET MASS
400 kg

53 cm

Proceed with bottom off-loading in the following manner using gravity flow or pump:

- In cold weather, apply steam to the bottom unloading connection and to the steam coil connection valves.
- Relieve internal pressure as previously mentioned.
- After connecting the unloading line to a 152 mm (6 in.) bottom outlet, open the inside bottom valve by turning the valve rod handle at the top of the car.
- Off-load the car by gravity or pump.

4.2.2 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in morpholine service. It is recognized that other materials may be used for particular applications, as indicated in Table 5. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets and pumps.

Schedule 40 seamless ASTM A106 carbon steel pipes and fittings lined with chlorinated polyether resins are recommended for morpholine lines (DCRG 1978). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak after a very short time. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipeline should be tested with air at pressures from 345 to 518 kPa (50 to 75 psi) and all leaks carefully stopped.

The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on morpholine tank cars; process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining.

Flexible bellows-type expansion joints should be used for the flexible sections of the unloading line. They are manufactured with ASA ductile iron flanges with expansion members molded from tetrafluoroethylene resin (Dow PPS 1972). Some installations of flexible line are made with standard lined fittings using a number of screwed elbows.

For valving, cast iron or cast steel diaphragm valves lined with chlorinated polyether or polyvinylidene fluoride resin will serve adequately (Dow PPS 1972). Viton may be used as a gasket material at normal temperature ranges (DCRG 1978).

A standard centrifugal pump with "wet end" material of carbon steel gives good results (PC 1982). Provision must be made for draining the pump so that repairs can be made safely. Rotary or centrifugal pumps of most types can be used, but should be fitted with externally lubricated bearings (Kirk-Othmer 1978).

Storage tanks of carbon steel are generally acceptable. For high colour standards, stainless steel 304 or 316 are more satisfactory. Morpholine reacts with copper and its alloys, thus these must be avoided in any fittings. Storage tanks should be blanketed with nitrogen to prevent absorption of water or acid gases from the air (Kirk-Othmer 1978).

4.3 Compatibility with Materials of Construction

The compatibility of morpholine with materials of construction is indicated in Table 5. The unbracketed abbreviations are described in Table 6. The rating system for this report is briefly described below.

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

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	All	24	Chlorinated Polyether PVDF (DCRG 1978)		
		66	PP (DCRG 1978)		
2. Pumps	All	Most	Ductile Iron CS, (PC 1982)		
3. Others	All	60	PE, PP, POM IIR, EPDM, CR FPM, CSM (GF)	uPVC (GF) Carbon Steels (Kirk-Othmer 1978)	NR NBR (GF) Copper Copper Alloys (Kirk-Othmer 1978)
		Most	Stainless steel (304 or 316) (Kirk-Othmer 1978)		
	100%	24 to 100	Glass (CDS 1967) SS 316 (ASS)		

TABLE 6 MATERIALS OF CONSTRUCTION

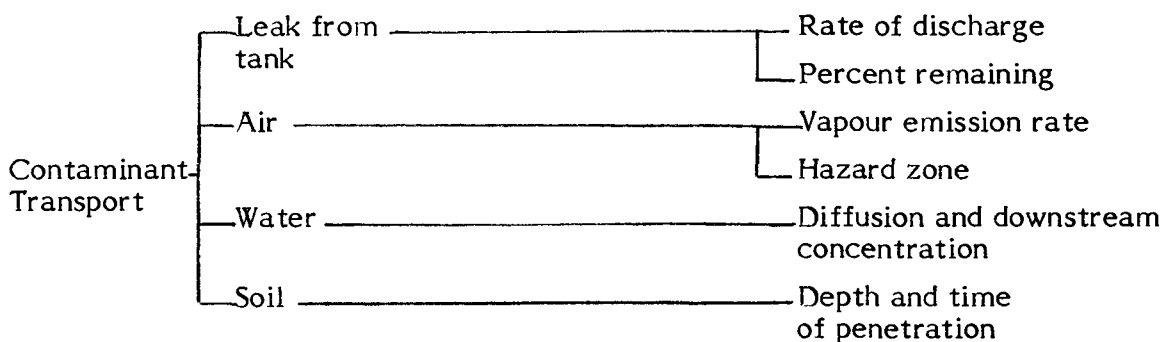
Abbreviation	Material of Construction
	Aluminum
	Chlorinated Polyether
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Copper
	Copper Alloys
	Ductile Iron
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene Rubber (Nitrile, Buna N)
NR	Natural Rubber
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVDF	Polyvinylidene Fluoride
SS (Followed by grade)	Stainless Steel
uPVC	Unplasticized Polyvinyl Chloride

5 CONTAMINANT TRANSPORT

5.1 General Summary

The vapour pressure of morpholine is sufficiently high that spills may release significant concentrations of vapour to the atmosphere. Since it is miscible with water and neutrally buoyant at 20°C, spills will also mix with water. When spilled on soil, the liquid will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may be an environmental concern.

The following factors are considered for the transport of a spill in the air, water and soil:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Morpholine is occasionally transported in railway tank cars as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size has been chosen throughout the EnviroTIPS series 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 morpholine is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the relatively low volatility of morpholine and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

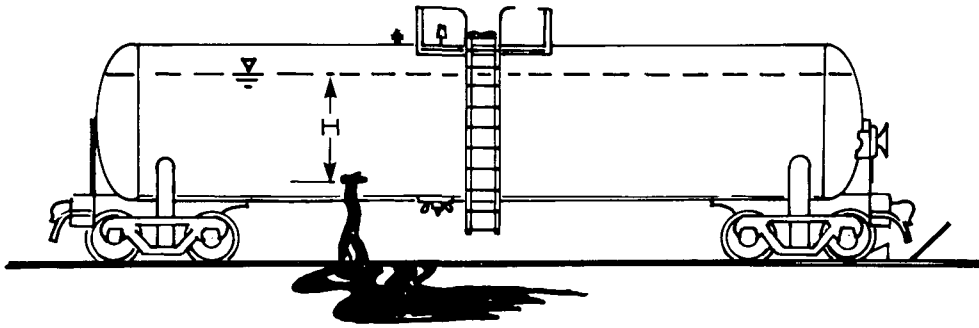


FIGURE 7 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

5.2.2 Nomograms.

5.2.2.1 Figure 8: Percent remaining versus time. Figure 8 provides a means of estimating the percent of liquid 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 is assumed to be initially full (at $t=0$) with a volume of about 80 000 L of morpholine. 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.

5.2.2.2 Figure 9: Discharge rate versus time. Figure 9 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

MORPHOLINE

PERCENT REMAINING
VS TIME

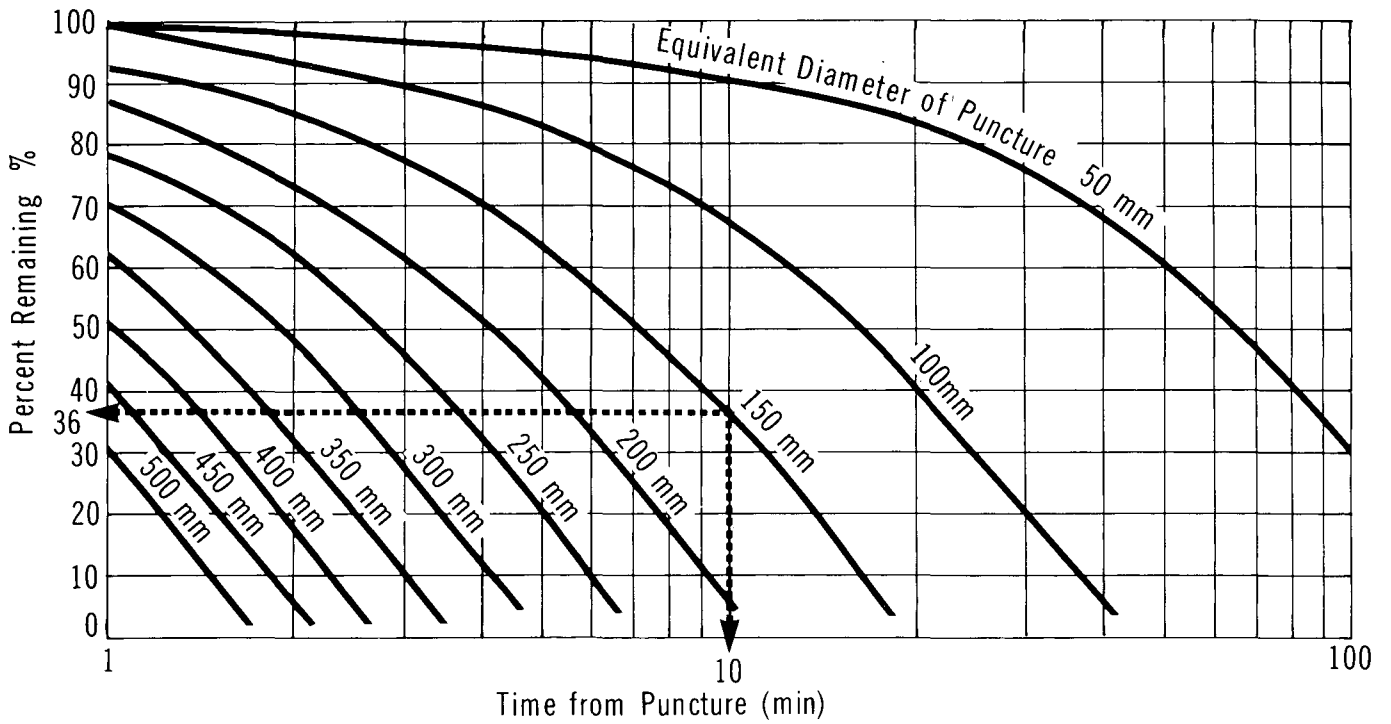
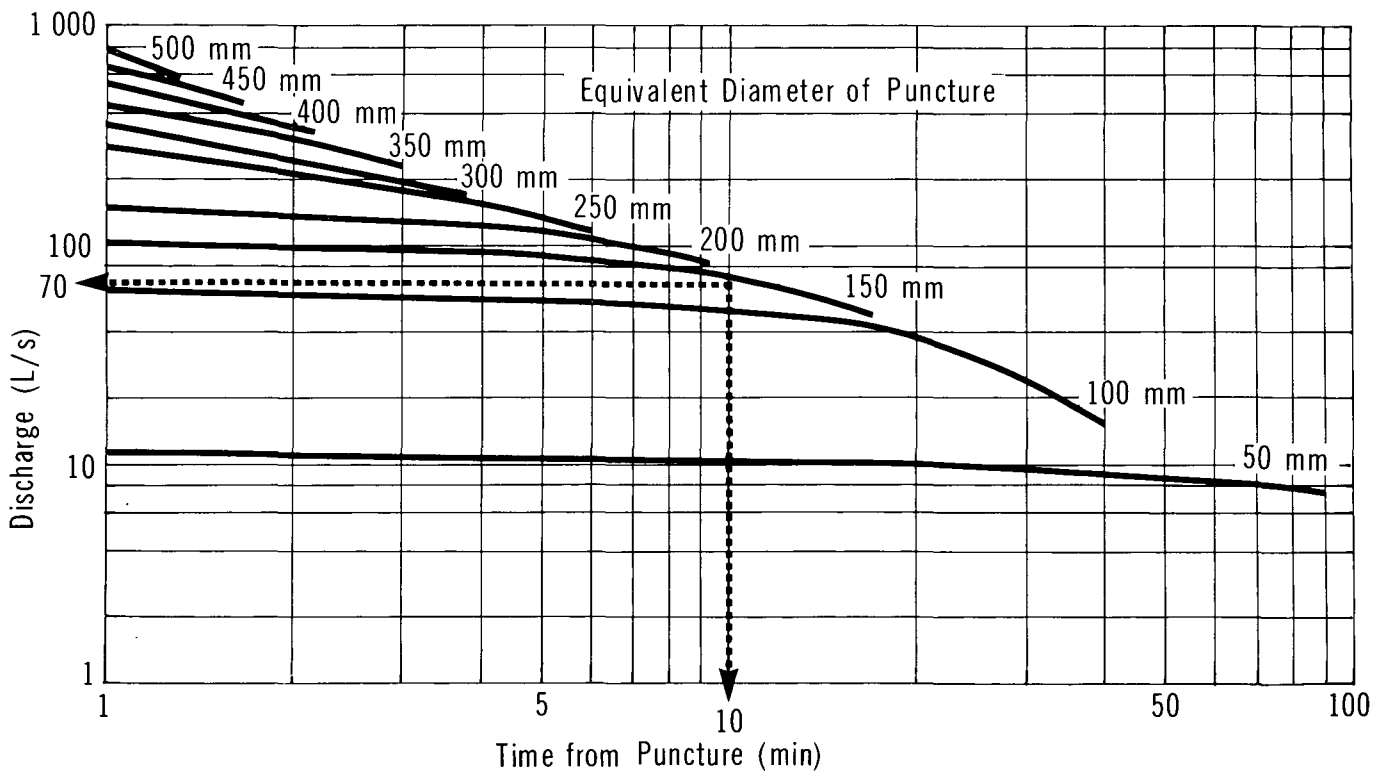


FIGURE 9

MORPHOLINE

DISCHARGE RATE
VS TIME



5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with morpholine 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 10 minutes?

Solution to Problem A

- . Use Figure 8
- . With $t=10$ min and $d=150$ mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- . Use Figure 9
- . With $t=10$ min and $d=150$ mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since morpholine is a liquid with a relatively low volatility, direct venting of the vapour to the atmosphere from a hole in a punctured vessel does not constitute a significant hazard downwind. Only vapour released from a liquid pool spilled on a ground or water surface is treated here.

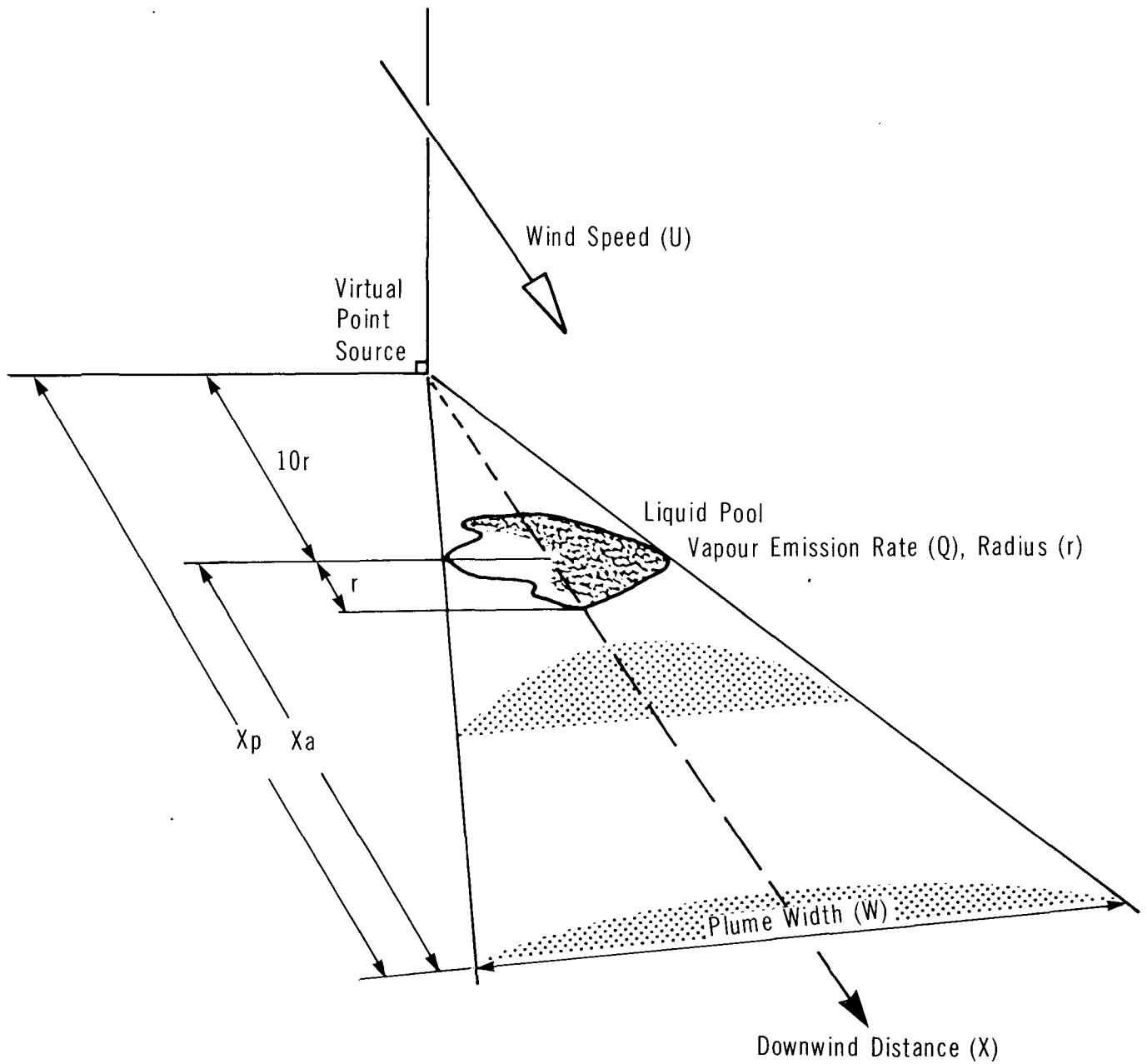
To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely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

Figure 10 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source as a virtual point source (with the same vapour emission rate, Q) located 10 equivalent pool radii upwind.

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.

MORPHOLINE

SCHEMATIC OF CONTAMINANT PLUME



The following nomograms and data tables are contained in this section (to be used in the order given):

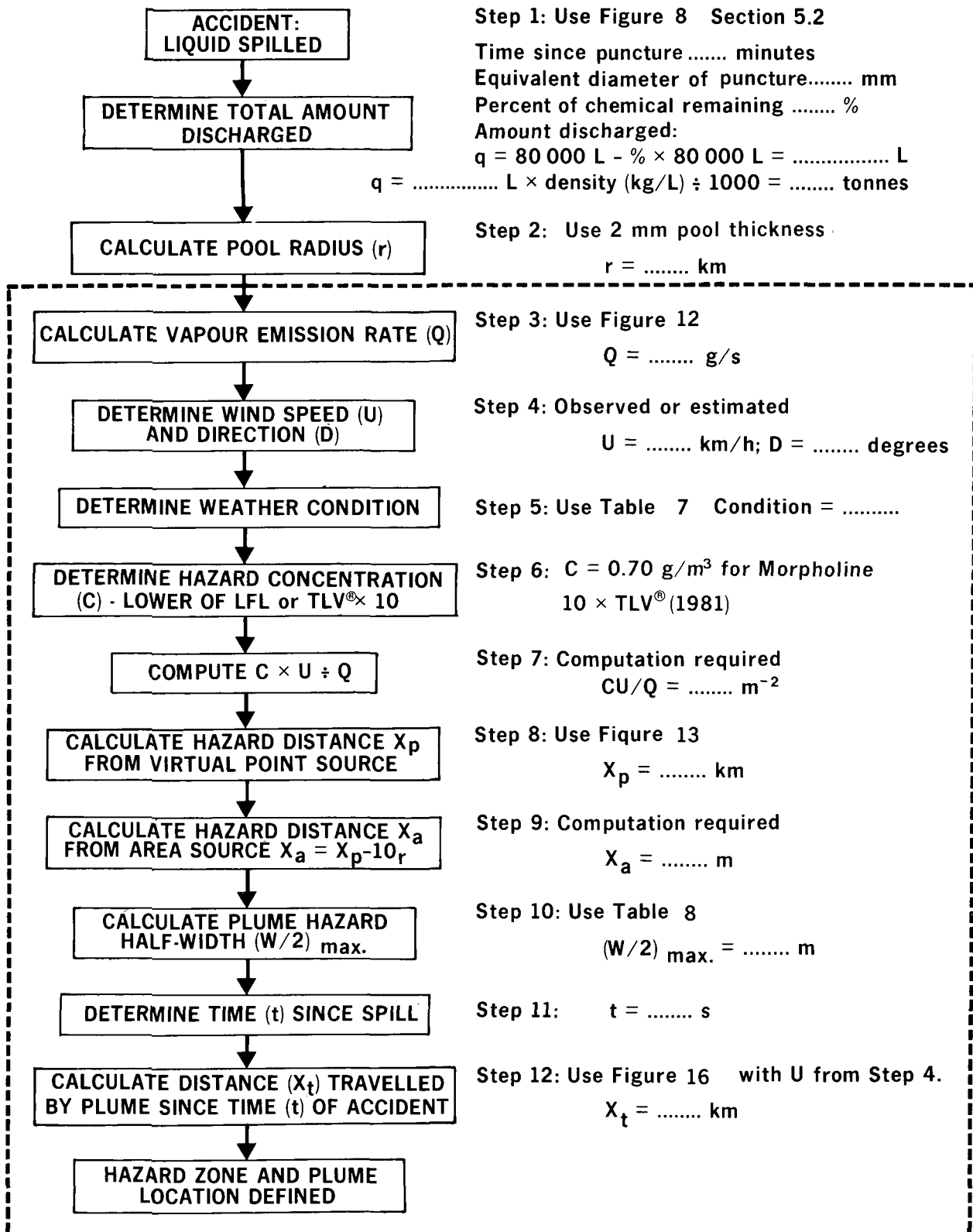
- Figure 12: vapour emission rate from a liquid pool as a function of maximum pool radius
- Table 7: weather conditions
- Figure 13: normalized vapour concentration as a function of downwind distance and weather conditions
- Table 8: maximum plume hazard half-widths
- Figure 16: vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 11 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 discharged" are contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 12: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for morpholine has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for morpholine at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 0.27 g/(m²s). Evaporation rates at other temperatures have been calculated using the evaporation rate equation which at a given wind speed is dependent on ambient temperature and the vapour pressure (CHRIS 1978) of morpholine at that temperature. For example, evaporation rates of 0.065 g/(m²s) at 0°C and 0.44 g/(m²s) at 30°C were calculated for a wind speed of 4.5 m/s.

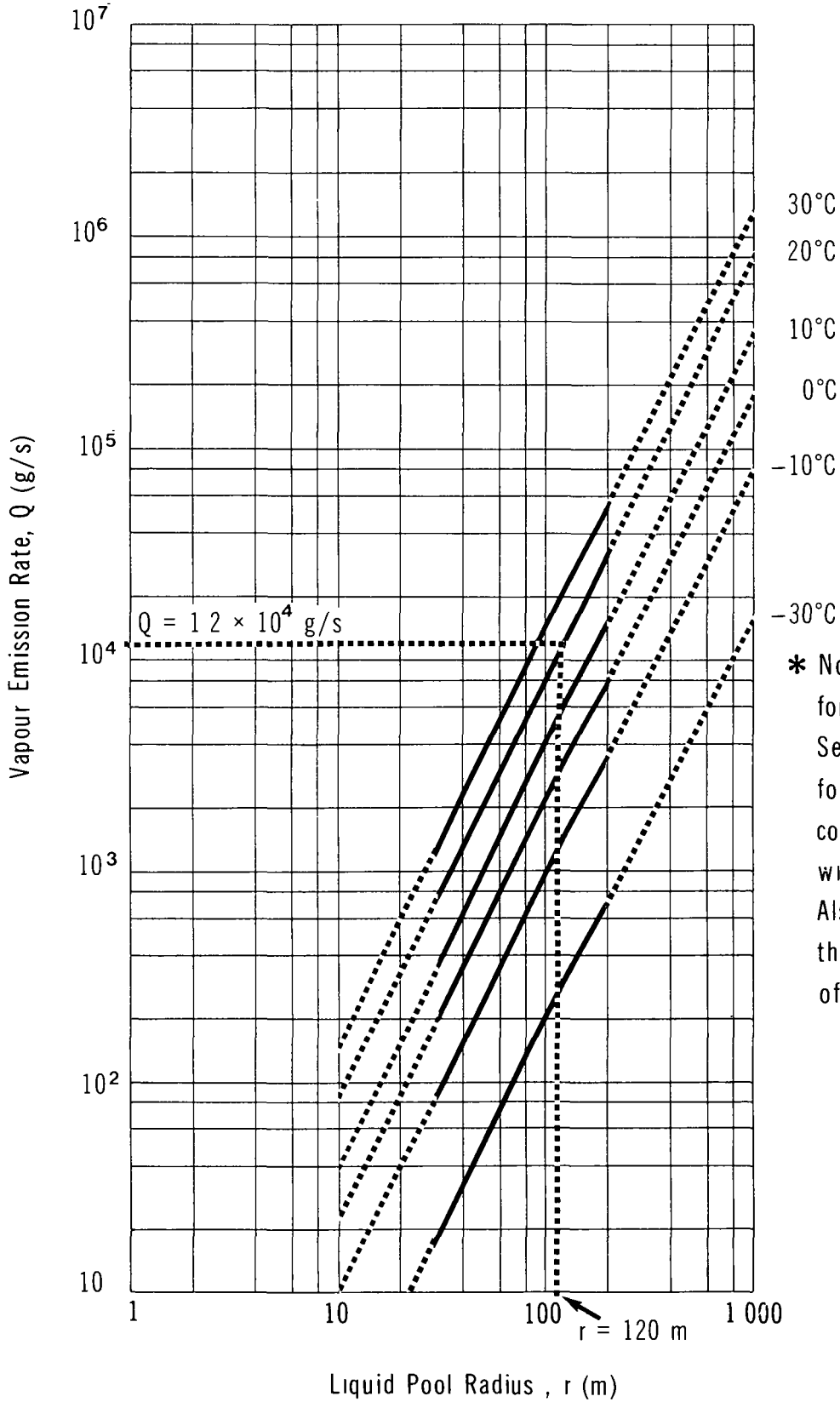
Use: For a pool of morpholine of known radius, the rate (Q) at which morpholine is released to the atmosphere at a given temperature can then be estimated from Figure 12. The solid portions of the curves represent spills of 0.3 to 80 tonnes, the latter representing about one standard 80 000 L rail car load of morpholine. It should be noted that Figure 12 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of morpholine vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

**FLOW CHART TO DETERMINE
VAPOUR HAZARD ZONE**



MORPHOLINE

VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES



* Note: Nomogram applies for wind speed of 4.5 m/s. See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.3 to 80 tonnes.

It should also be noted that the determination of the emission rate is based on the spill radius on calm water (Table VI, CHRIS 1974). The spill radius employed was arbitrarily chosen as an intermediate value between that of benzene (a moderately volatile liquid) and that of iso-amyl nitrite (a nonvolatile liquid). This model situation was chosen to apply for water-soluble liquids with boiling points above ambient temperature, and to a limited number of water-soluble and water-insoluble organic liquids that are not treated by CHRIS (CHRIS 1974). Since calm water represents a flat, unbounded surface compared to the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous), the spill radius on calm water is considered to provide the maximum value. Therefore, when spills on land are assessed by using the water algorithm, the spill radius would be overestimated and worst case values are provided.

5.3.2.2 Figure 13: Normalized vapour concentration versus downwind distance.

Figure 13 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 (CU/Q) at the centreline of the contaminant plume. 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 13, the weather condition must be determined from Table 7.

TABLE 7 WEATHER CONDITIONS

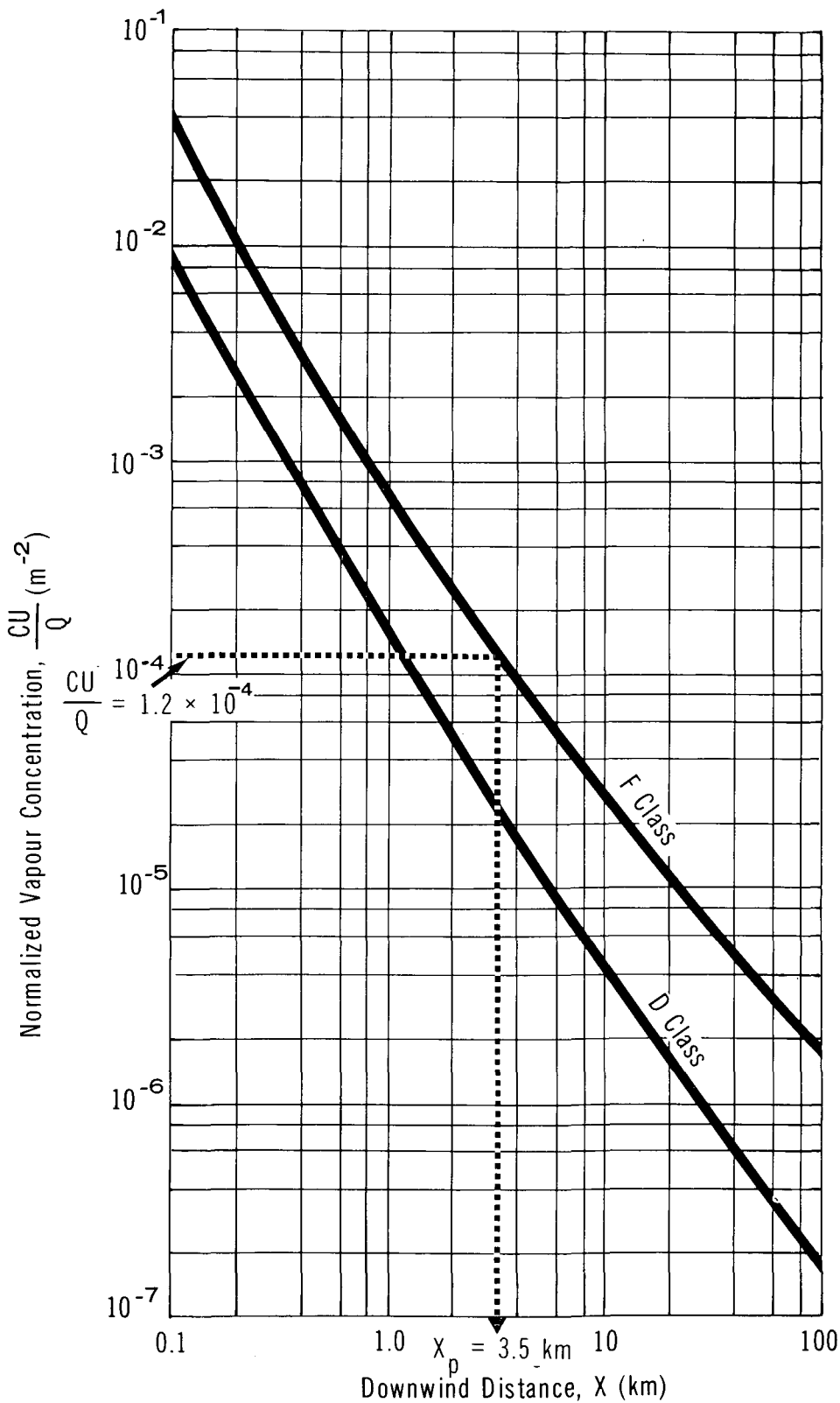
Weather Condition F	Weather Condition D
Wind speed < 11 km/h (≈ 3 m/s) and one of the following: <ul style="list-style-type: none"> - overcast day - night time - severe temperature inversion 	Most other weather conditions

Use: The maximum hazard distance, X_p , downwind of the spill can be calculated from Figure 13 knowing:

- Q , the vapour emission rate (g/s)
- U , the wind speed (m/s)
- the weather condition

MORPHOLINE

**NORMALIZED VAPOUR CONCENTRATION
VS DOWNWIND DISTANCE**



- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value (TLV[®], in g/m³), or the Lower Flammability Limit (LFL, in g/m³). Note: To convert the TLV[®] (in ppm) and the LFL (in percent by volume) to concentrations in g/m³, use Figures 14 and 15

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 large hazard zones.

5.3.2.3 Table 8: Maximum plume hazard half-widths. This table presents data on the maximum plume hazard half-width, $(W/2)_{\max}$, for a range of Q/U 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 morpholine Threshold Limit Value (TLV[®]) of 0.07 g/m³, or 0.70 g/m³. The maximum plume hazard half-width represents the maximum half-width of the morpholine vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV[®]. Table 8 is therefore only applicable for a morpholine hazard concentration limit of 10 x TLV[®] or 0.70 g/m³. Also, data are provided up to a maximum hazard distance downwind of 100 km.

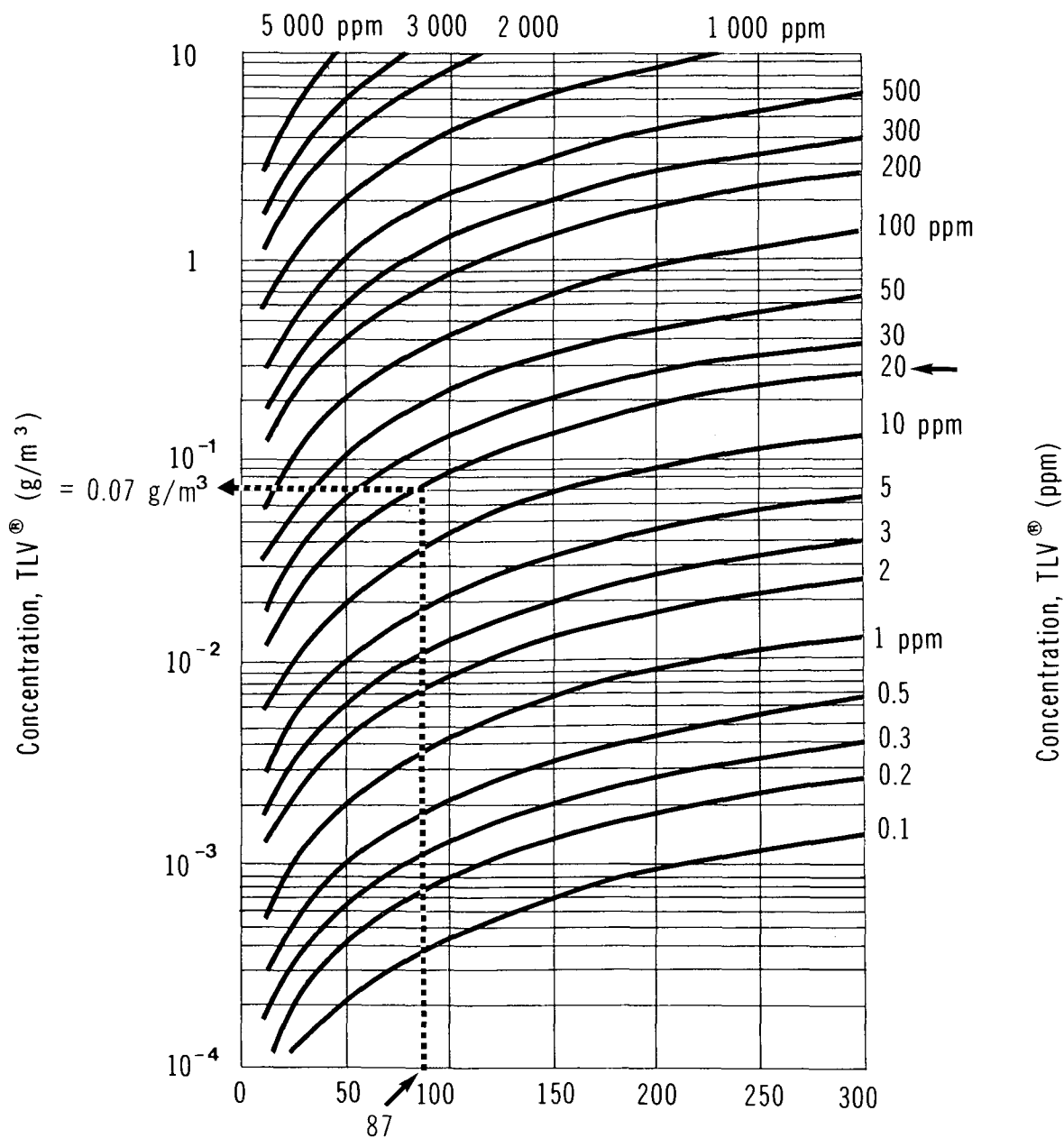
Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 15 000 to 4 500 000 g/s, corresponding to morpholine spills in the range of about 40 to greater than 8000 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 80 000 kg or approximately 80 tonnes. Therefore, under class D of Table 8, data are provided for up to about 100 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 1500 to 450 000 g/s, corresponding to morpholine spills in the range of about 1 to 5500 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 69 times a standard rail car load.

Use: Knowing the weather condition, Q and U, compute Q/U. Choose the closest Q/U value in the table and the corresponding $(W/2)_{\max}$, the maximum plume hazard half-width, in metres. (For an intermediate value, interpolate Q/U and $(W/2)_{\max}$ values.) Also refer to the example at the bottom of Table 8.

MORPHOLINE

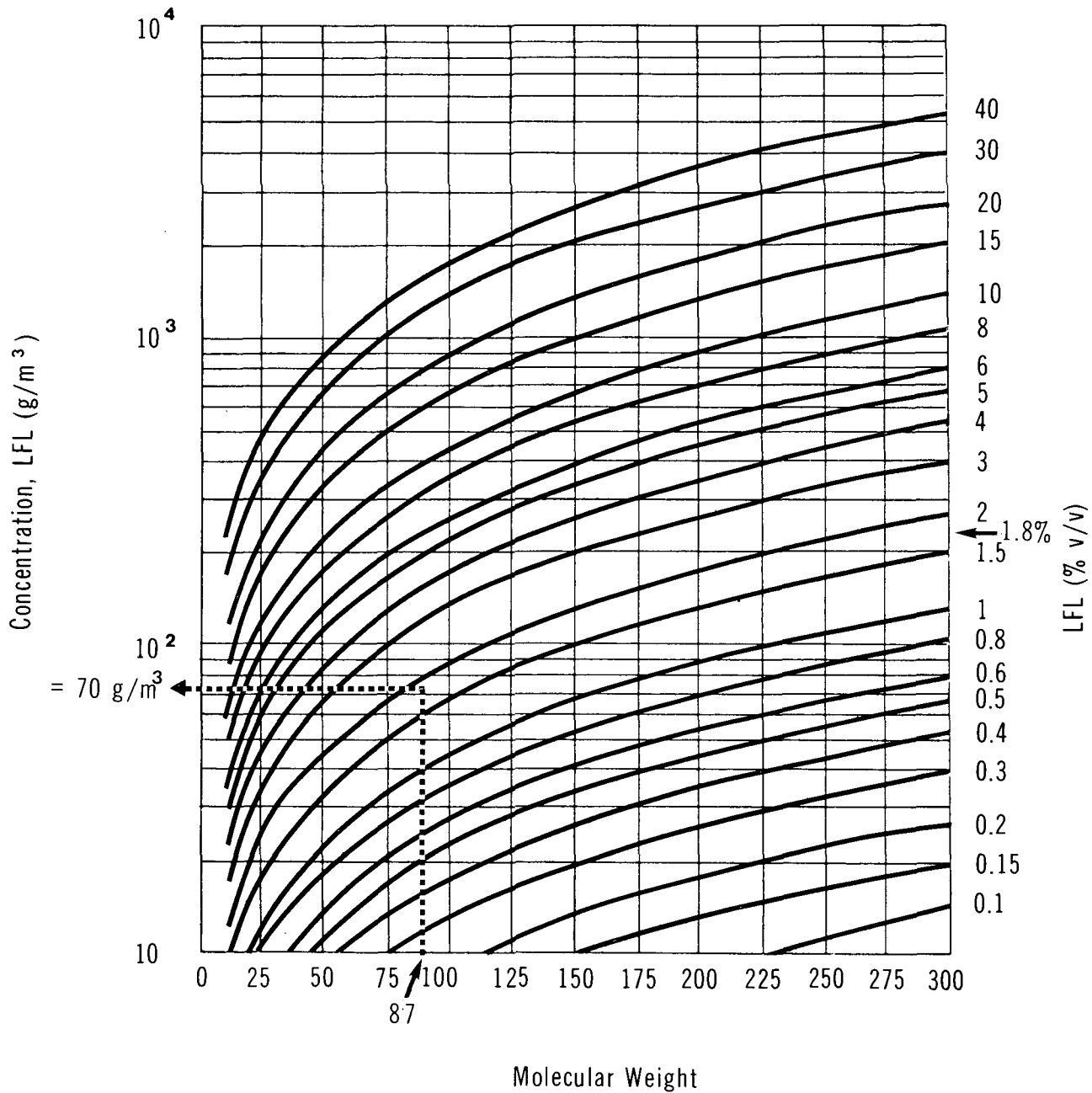
CONVERSION OF THRESHOLD LIMIT VALUE
(TLV[®]) UNITS (ppm to g/m³)



Molecular Weight
 Example: Morpholine, MW = 87, TLV[®] = 20 ppm
 then TLV[®] in g/m³ = 0.07

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

MORPHOLINE

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


Example: Morpholine, MW = 87, LFL = 1.8% then LFL in g/m³ = 70

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

TABLE 8 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR MORPHOLINE AT 20°C)

Weather Condition D		Weather Condition F	
Q/U (g/m)	(W/2) _{max} (m)	Q/U (g/m)	(W/2) _{max} (m)
4 500 000	3250 (99.5 km)*	450 000	1510 (99.5 km)*
4 000 000	3025	400 000	1380
3 500 000	2785	300 000	1115
3 000 000	2530	250 000	970
2 500 000	2260	200 000	825
2 000 000	1970	150 000	665
1 500 000	1650	125 000	580
1 000 000	1280	100 000	490
750 000	1075	75 000	395
500 000	835	50 000	300
400 000	730	25 000	195
300 000	610	10 000	110
200 000	485	7 500	90
150 000	410	5 000	70
125 000	370	2 500	45
100 000	325	1 000	30
75 000	275	500	20
50 000	215		
25 000	145		
10 000	85		
5 000	60		
2 500	40		
1 000	25		
500	20		

Q/U = 5715 → (W/2)_{max} = 80 m

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

Example: A spill releasing morpholine vapour at the rate of $Q = 1.2 \times 10^4$ g/s under weather condition F and a wind speed $U = 2.1$ m/s means $Q/U = 5715$ g/m which results in a maximum plume hazard half-width $(W/2)_{\max} = 80$ m.

Note: Above table is valid only for an morpholine concentration of $10 \times \text{TLV}^\circ$, or 0.70 g/m³.

5.3.2.4 Figure 16: Plume travel time versus travel distance. Figure 16 presents plots of plume travel time (t) versus plume 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 plume has travelled.

5.3.3 Sample Calculation. The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid morpholine. 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 apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill radius) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of morpholine 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.

Solution:

Step 1: Quantity spilled is given, $q = 20$ tonnes

Step 2: Determine the pool radius (r) for a spill of 20 tonnes

- Use observed (measured) pool radius if possible. If not, use the maximum radius calculated assuming a 2 mm spill thickness
- Radius (r) = 120 m \div 1000 = 0.12 km

Step 3: Calculate the vapour emission rate (Q) at $T = 20^\circ\text{C}$

- From Figure 12, for $r = 120$ m and $T = 20^\circ\text{C}$, $Q = 1.2 \times 10^4$ g/s

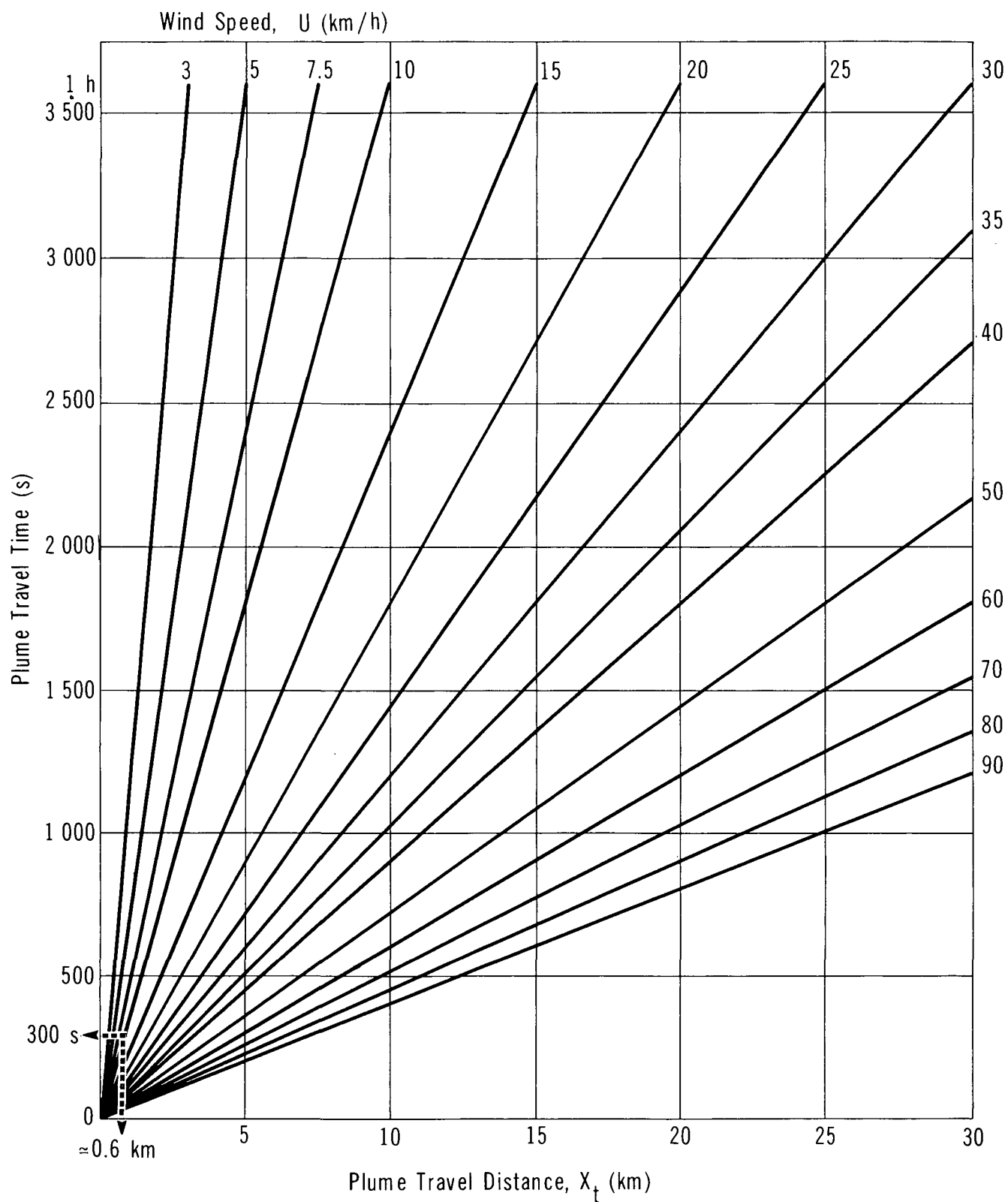
Step 4: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given:
 - $U = 7.5$ km/h, then $U = 7.5 \div 3.6 = 2.1$ m/s
 - $D = \text{NW}$ or 315° ($D = \text{Direction from which wind is blowing}$)

Step 5: Determine the weather condition

- From Table 7, weather condition = F since U is less than 11 km/h and it is night

MORPHOLINE

PLUME TRAVEL TIME
VS TRAVEL DISTANCE

- Step 6: Determine the hazard concentration limit (C)
- This is the lower of 10 times the TLV^o, or the LFL, so for morpholine
 $C = 0.70 \text{ g/m}^3$ (TLV^o = 0.07 g/m³; LFL = 70 g/m³)
- Step 7: Compute CU/Q
- $$CU/Q = \frac{0.70 \times 2.1}{1.2 \times 10^4} = 1.23 \times 10^{-4} \text{ m}^{-2}$$
- Step 8: Calculate the downwind distance (X_p) from the virtual point source
- From Figure 13, with $CU/Q = 1.2 \times 10^{-4} \text{ m}^{-2}$ and weather condition F,
 $X_p \approx 3.5 \text{ km}$
- Step 9: Calculate the hazard distance (X_a) downwind of the area source
- With $X_p = 3.5 \text{ km}$ and $r = 0.12 \text{ km}$, then $X_a = X_p - 10r =$
 $3.5 \text{ km} - 10(0.12 \text{ km}) = 2.3 \text{ km}$
- Step 10: Calculate the plume hazard half-width ($(W/2)_{\max}$)
- Use Table 8
 - With $Q = 1.2 \times 10^4 \text{ g/s}$ and $U = 2.1 \text{ m/s}$

$$\text{then } Q/U = \frac{1.2 \times 10^4}{2.1} = 5715 \text{ g/m}$$
 - Then for weather condition F, the closest Q/U value is between 5000 and 7500 g/m, which gives $(W/2)_{\max} \approx 80 \text{ m}$
- Step 11: Determine the time since the spill
- $t = 5 \text{ min} \times 60 = 300 \text{ s}$
- Step 12: Calculate the distance travelled (X_t) by the vapour plume since the time of the accident
- Using Figure 16 with $t = 300 \text{ s}$ and $U = 7.5 \text{ km/h}$, then $X_t = 0.6 \text{ km}$ (more accurately from $Ut = 2.1 \text{ m/s} \times 300 \text{ s} = 630 \text{ m} = 0.63 \text{ km}$)
- Step 13: Map the hazard zone
- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (80 m) by the hazard distance downwind of the area source (2.3 km) along the direction of the wind, as shown in Figure 17
 - If the wind is reported to be fluctuating by 20° about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 18

MORPHOLINE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

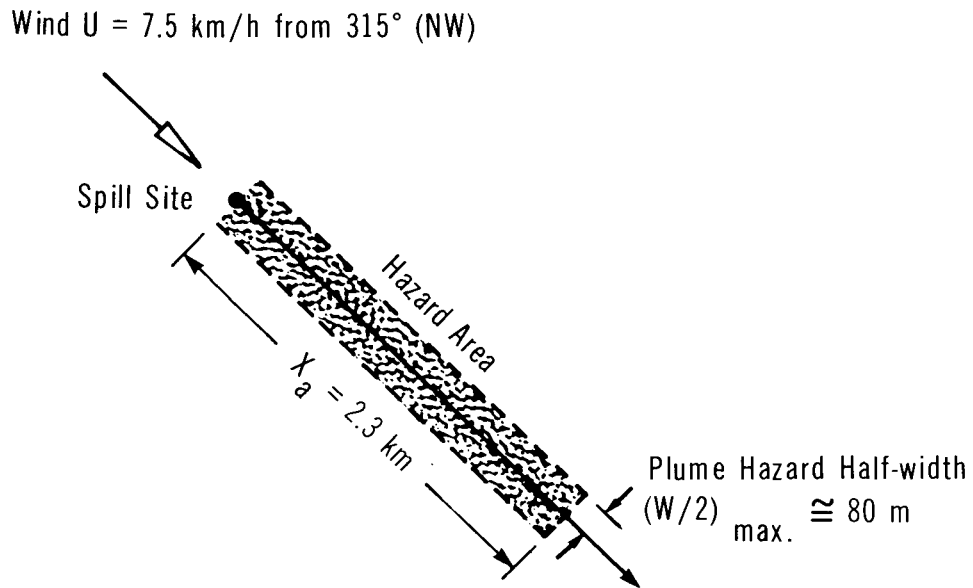
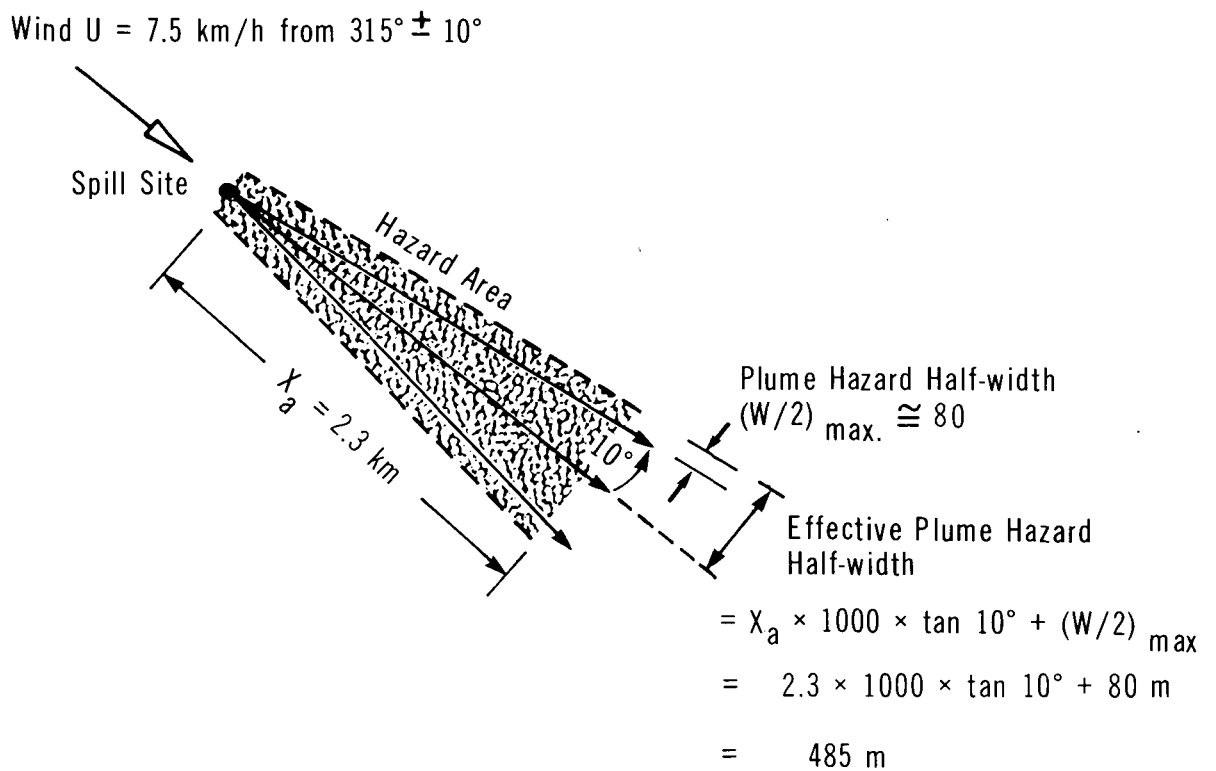


FIGURE 18

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HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM



- Note that the plume has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 13 minutes before the plume reaches the maximum downwind hazard distance of 2.3 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, morpholine will mix with the water and be 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 and therefore is well suited to modelling a spill of morpholine.

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.

5.4.2 Nomograms. The following nomograms are presented to calculate concentrations in non-tidal rivers and in lakes (still water).

Non-tidal Rivers

- Figure 20: time versus distance for a range of average stream velocities
- Figure 21: hydraulic radius versus channel width for a range of stream depths
- Figure 22: diffusion coefficient versus hydraulic radius for a range of average stream velocities
- Figure 23: α^* versus diffusion coefficient for various time intervals
- Figure 24: α versus δ^* for a range of spill sizes
- Figure 25: maximum concentration versus δ for a range of river cross-sectional areas

Lakes or Still Water Bodies

- Figure 26: volume versus radius for the hazard zone for a range of lake depths
 Figure 27: average concentration versus volume for the hazard zone for a range of spill sizes

The flowchart in Figure 19 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 20 through 27) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 20: Time versus distance. Figure 20 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 20.

Figure 21: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration 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 longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 21 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 22: Diffusion coefficient versus hydraulic radius. Figure 22 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 21 and the average stream velocity (U).

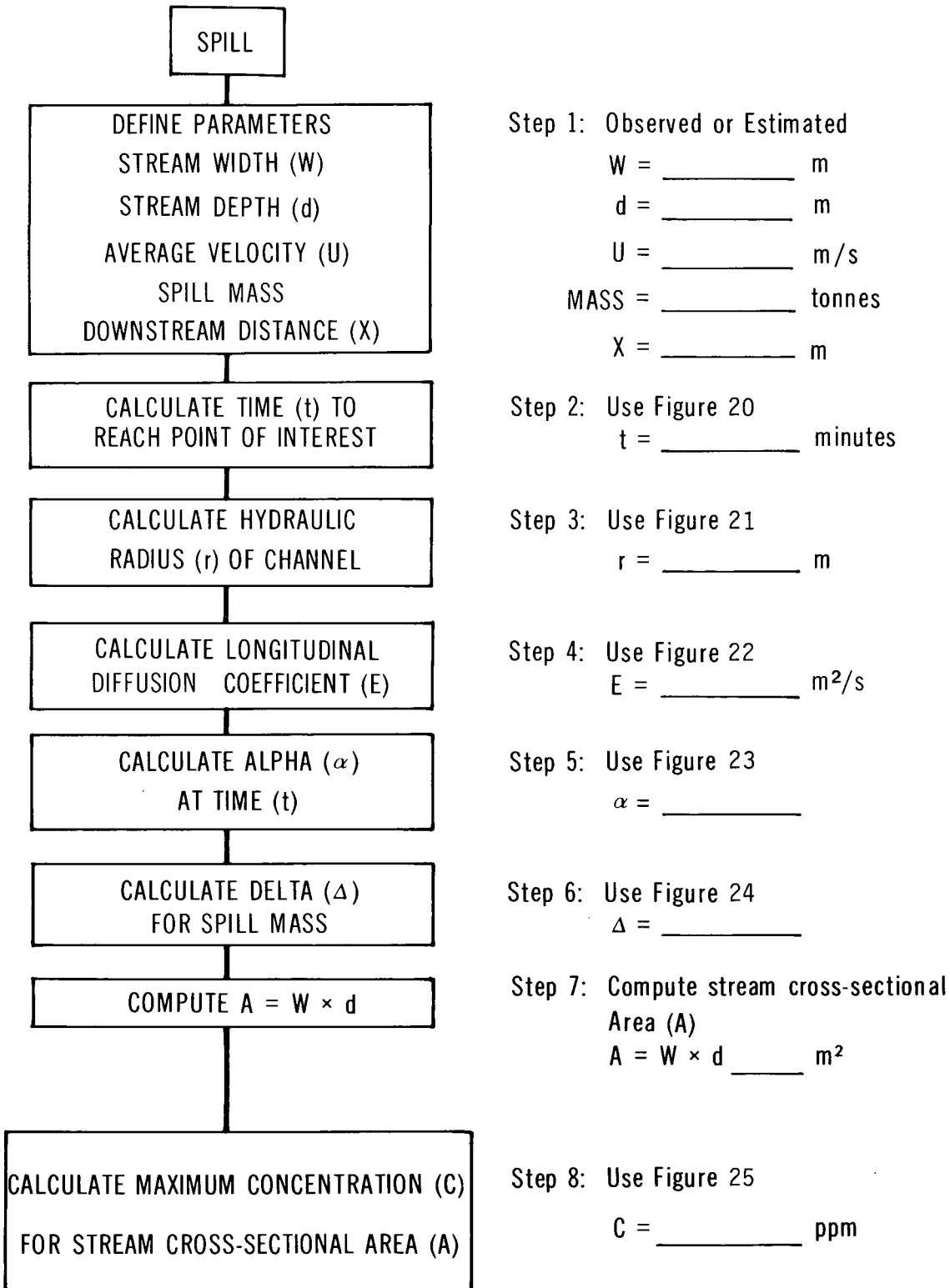
Figure 23: Alpha versus diffusion coefficient. Figure 23 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 24: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 24 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

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

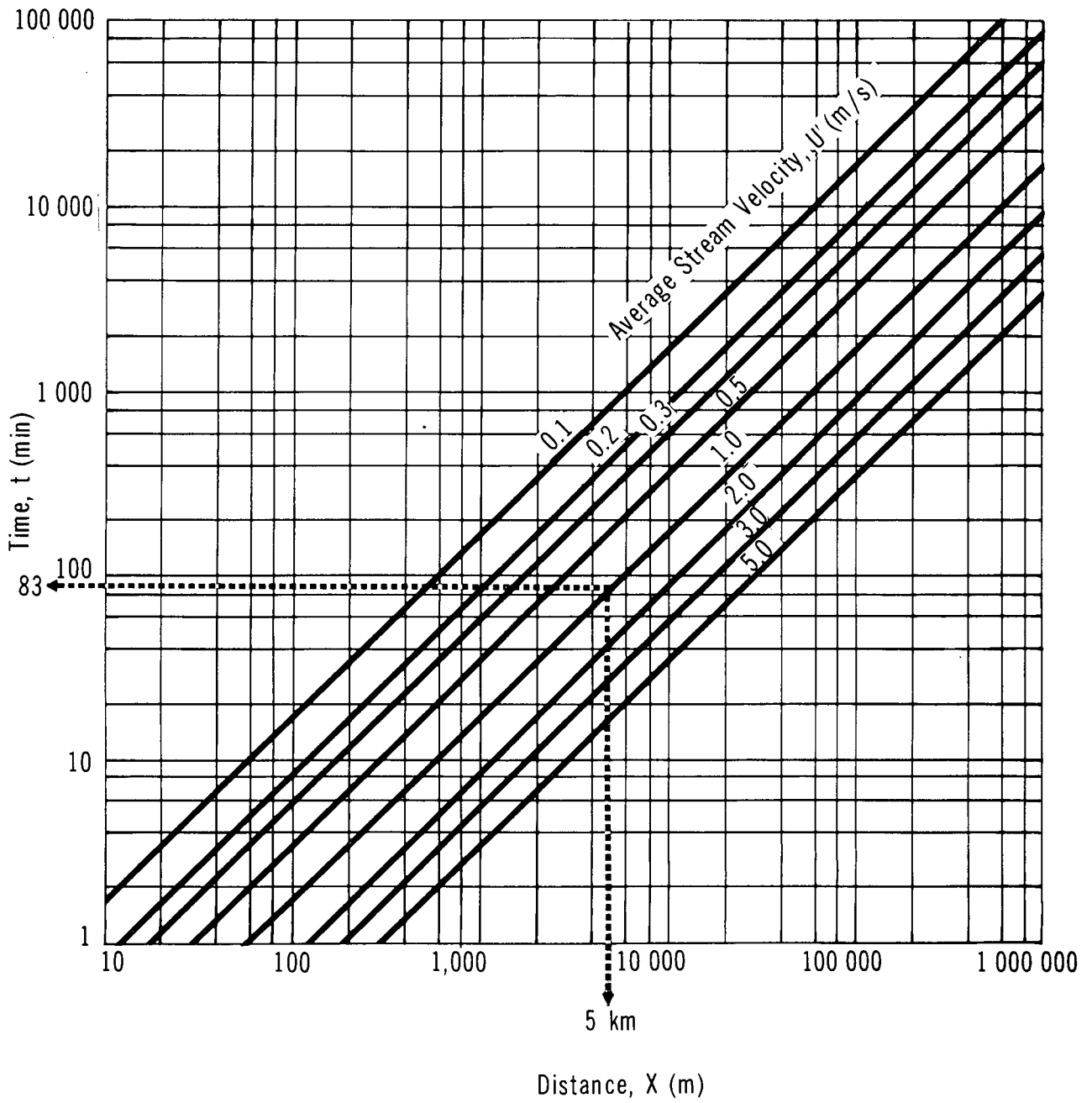
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FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS



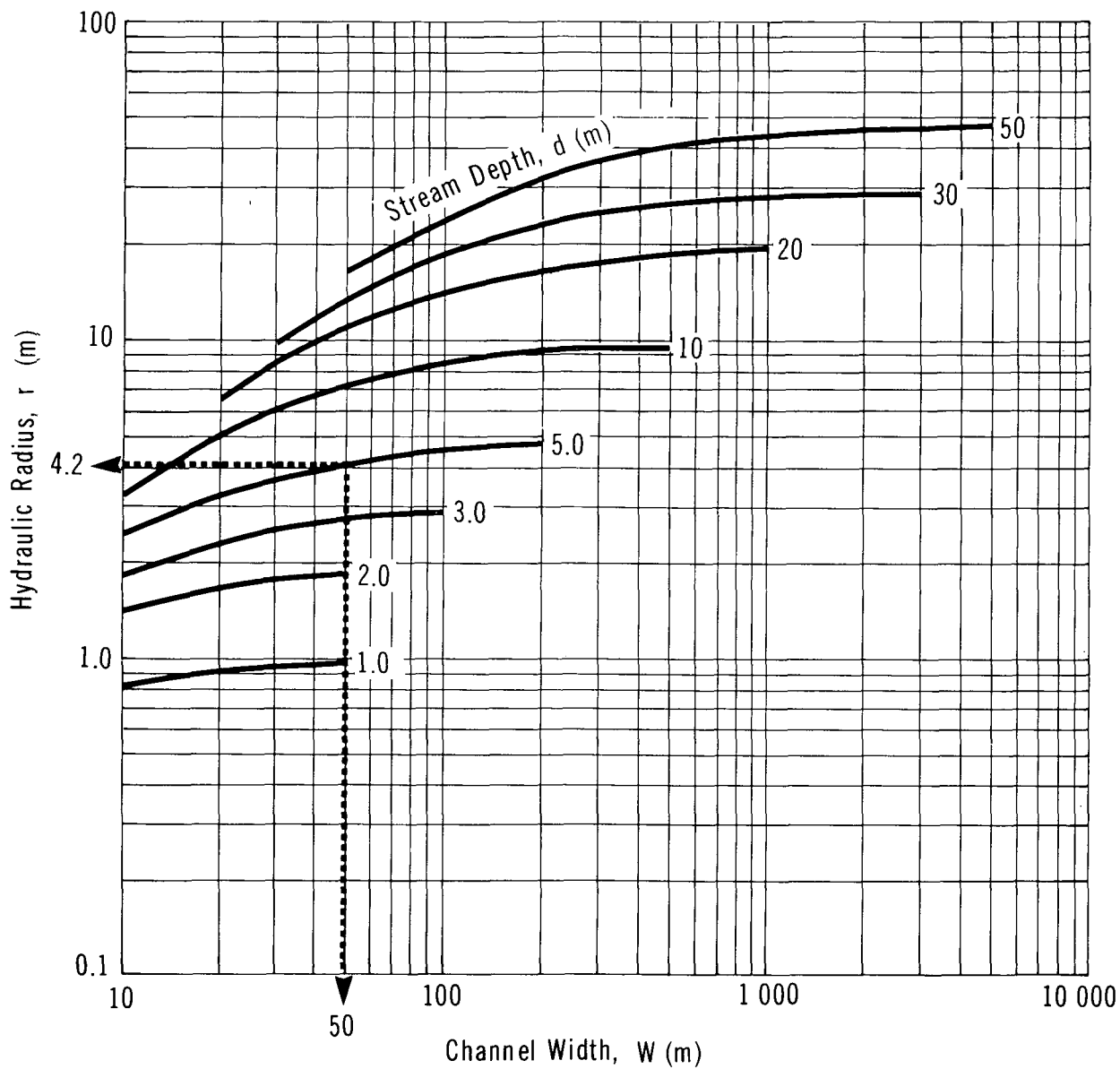
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TIME vs DISTANCE



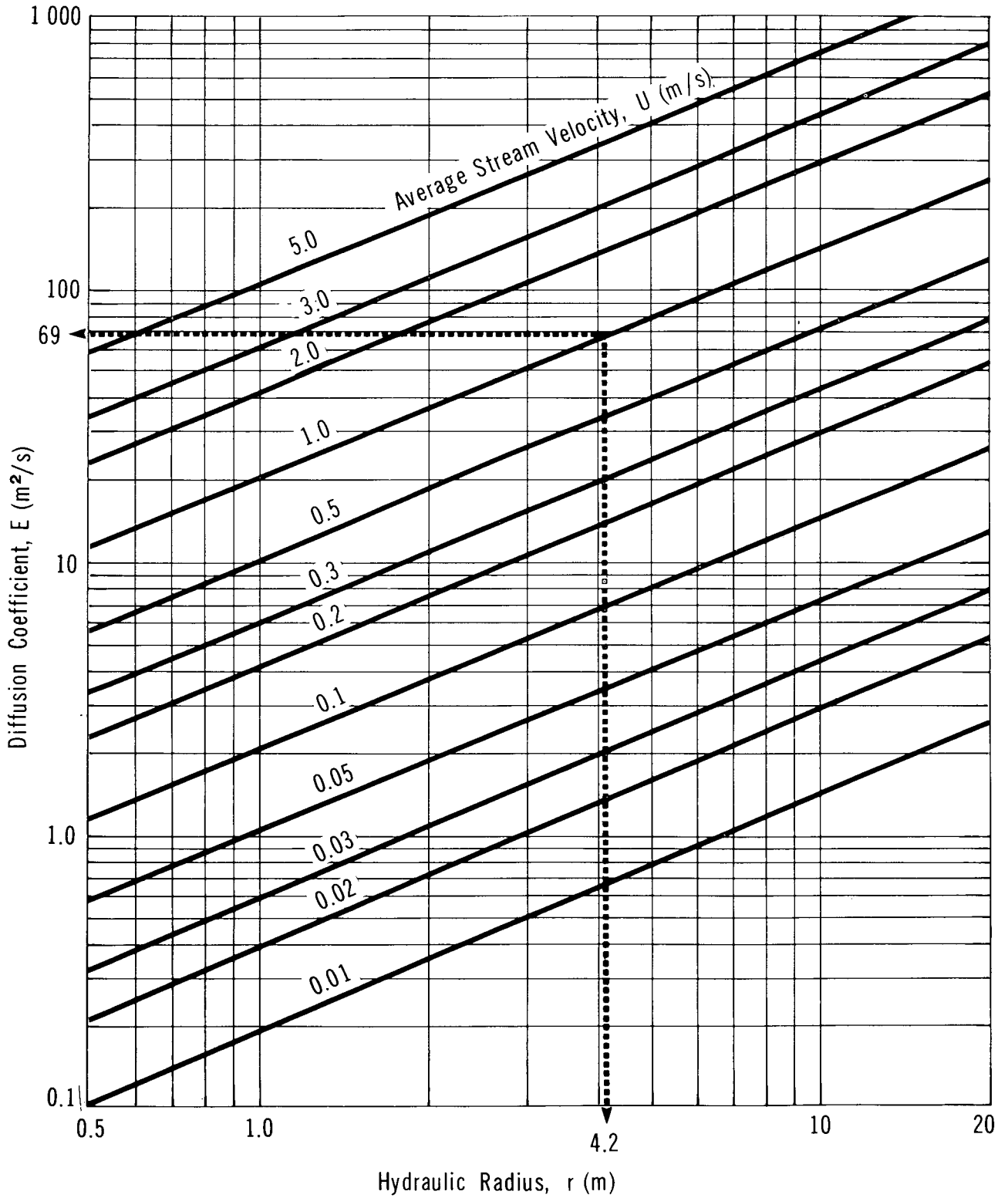
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HYDRAULIC RADIUS VS CHANNEL WIDTH



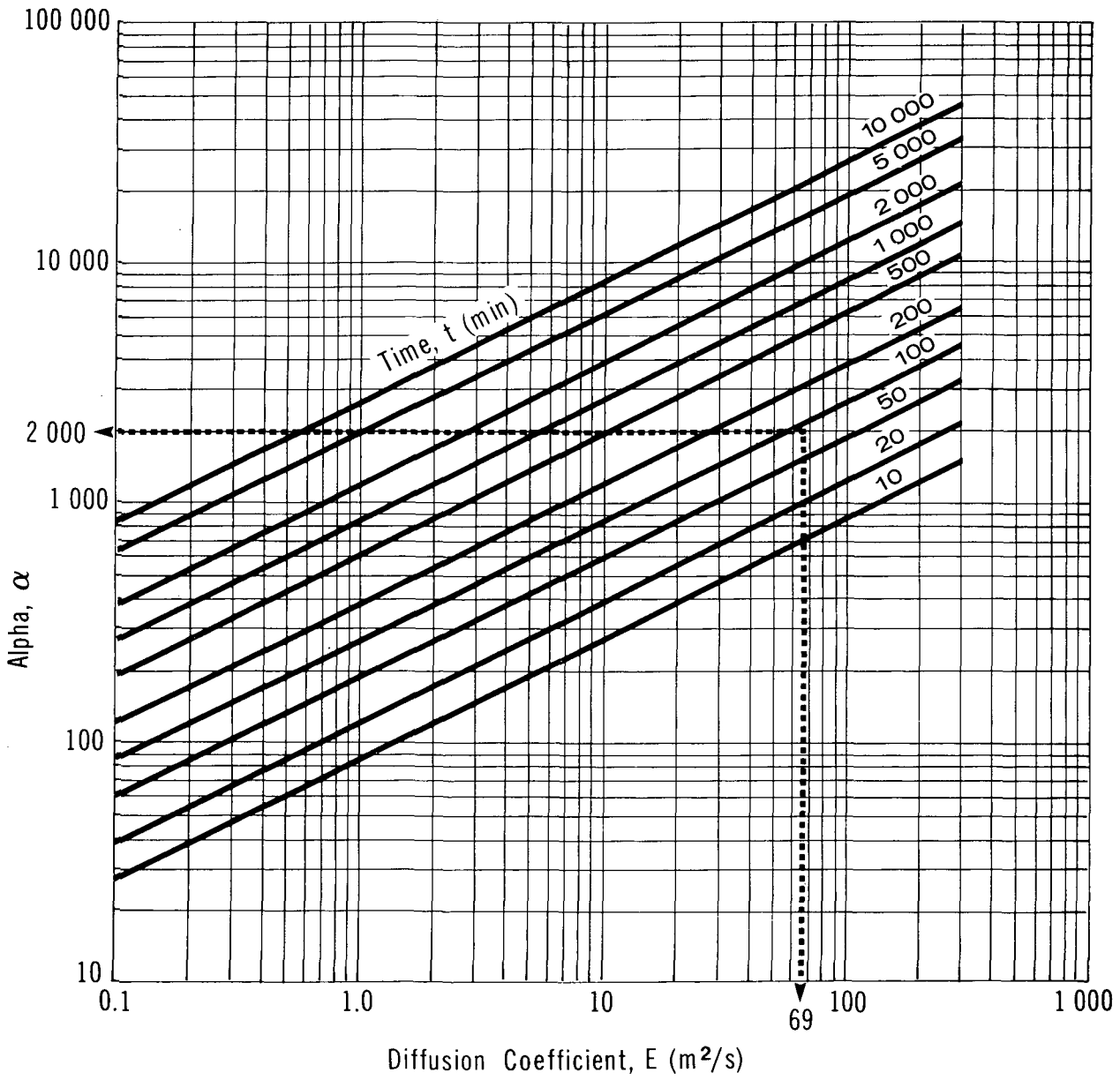
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DIFFUSION COEFFICIENT
VS HYDRAULIC RADIUS



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ALPHA vs DIFFUSION COEFFICIENT



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ALPHA vs DELTA

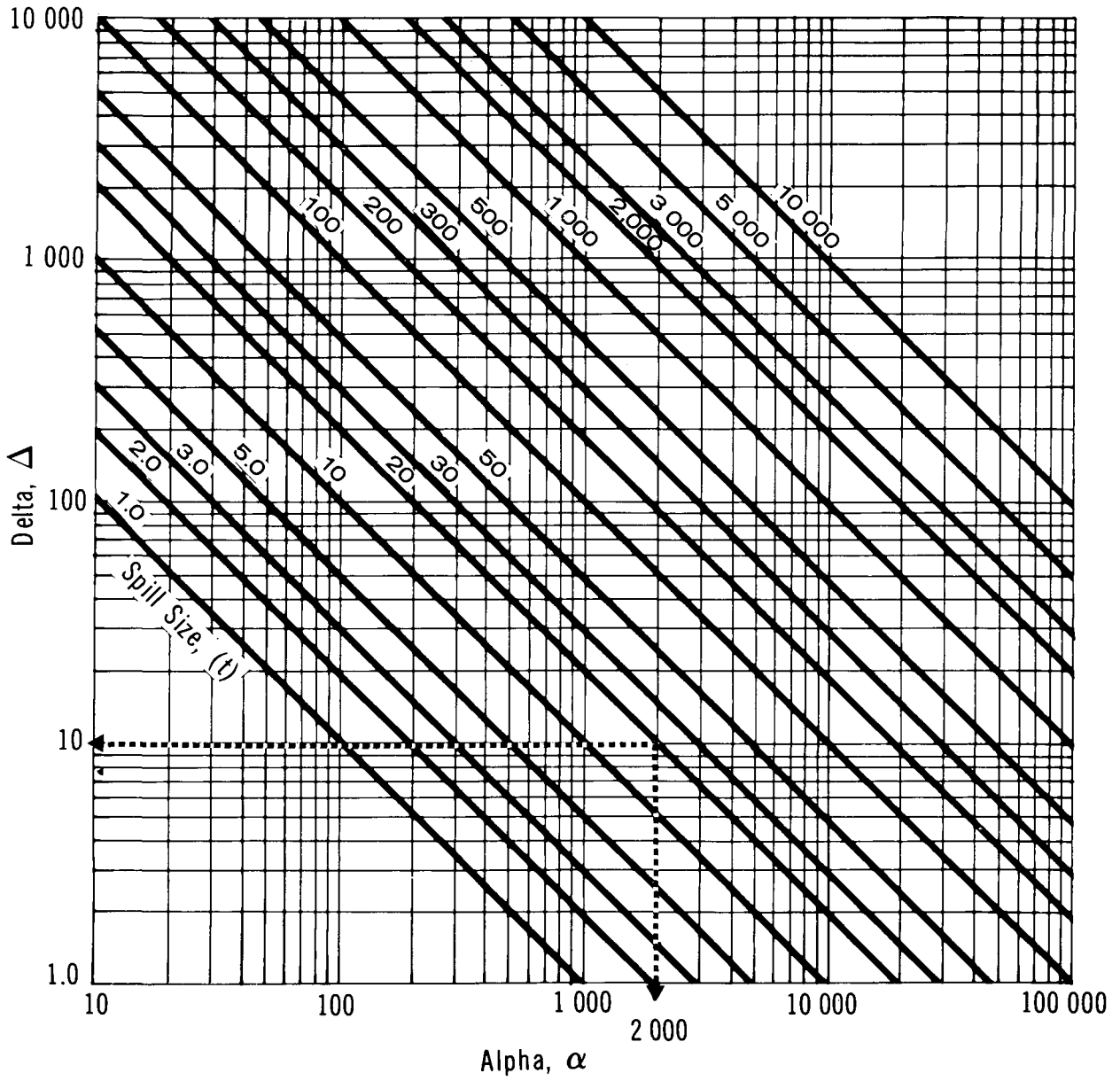


Figure 25: Maximum concentration versus delta. Figure 25 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 25 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.2.2 Nomograms for lakes or still water bodies.

Figure 26: 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 in the cylinder can be obtained from Figure 26. The radius (r) represents the distance from the spill to the point of interest.

Figure 27: 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 27 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.

5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal rivers. A 20 tonne spill of morpholine 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

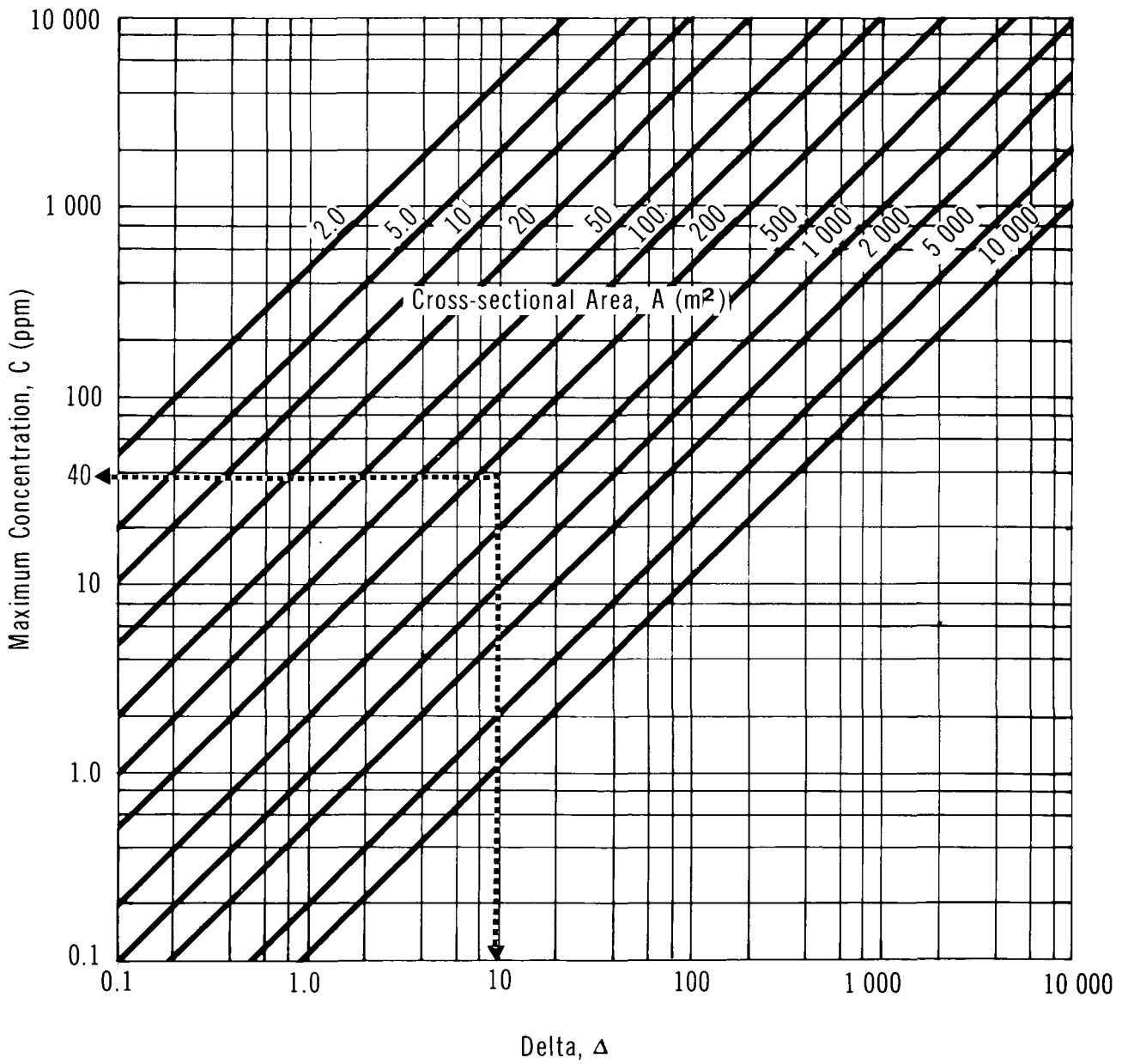
- $W = 50 \text{ m}$
- $d = 5 \text{ m}$
- $U = 1 \text{ m/s}$
- Spill mass = 20 tonnes of morpholine

Step 2: Calculate the time to reach the point of interest

- Use Figure 20
- With $X = 5000 \text{ m}$ and $U = 1 \text{ m/s}$, $t = 83 \text{ min}$

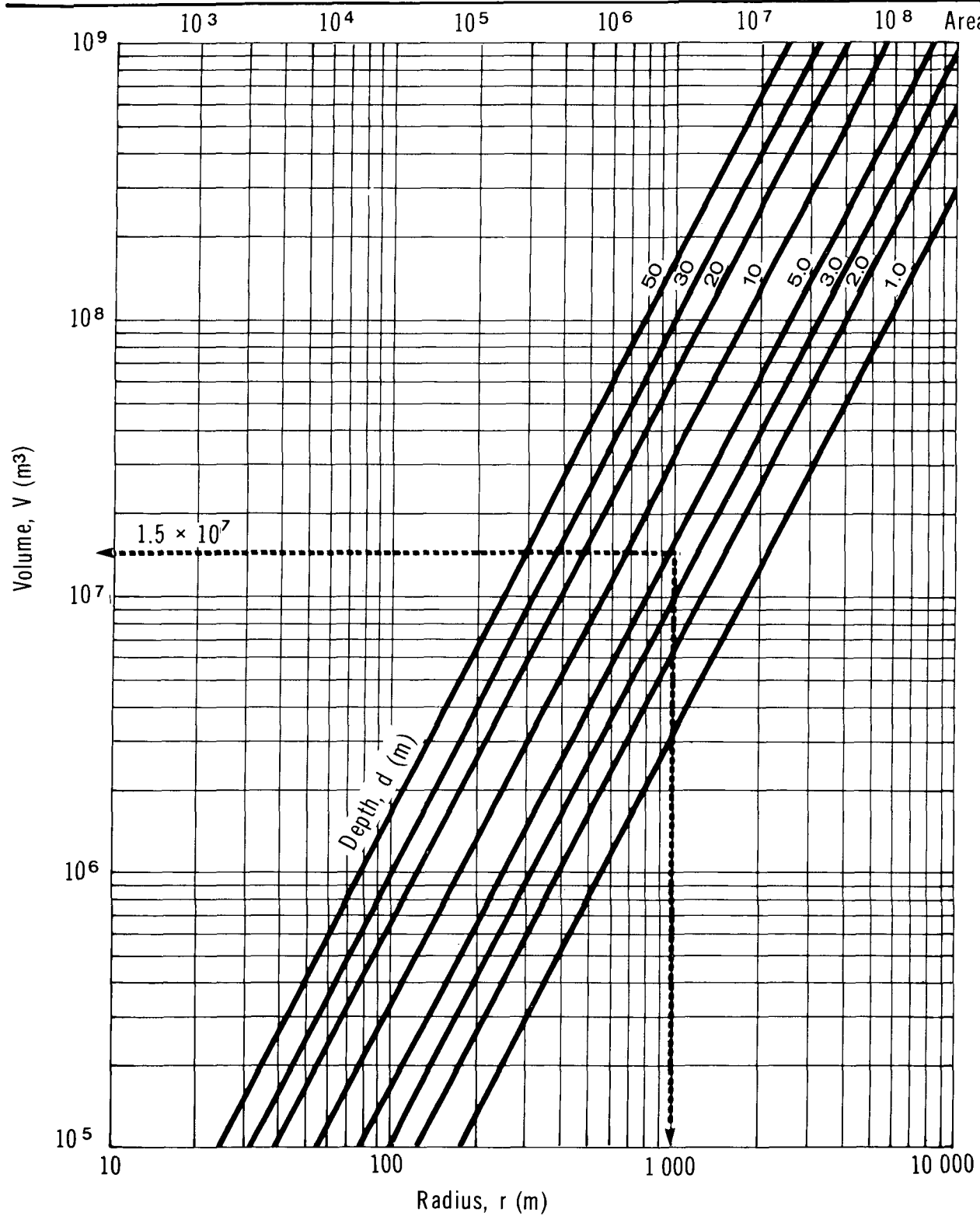
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MAXIMUM CONCENTRATION vs DELTA



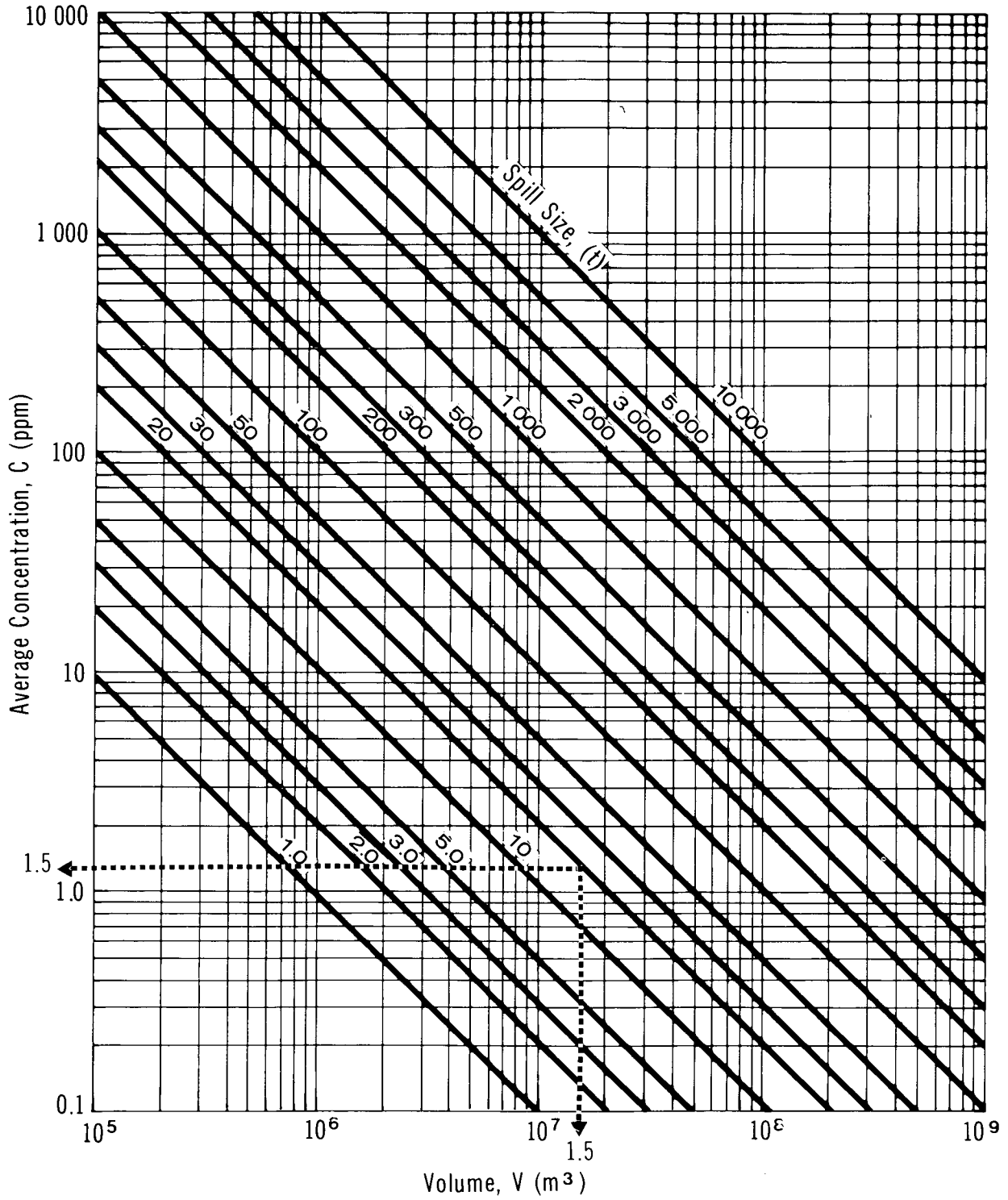
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VOLUME vs RADIUS



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AVERAGE CONCENTRATION vs VOLUME



- Step 3: Calculate the hydraulic radius (r)
- Use Figure 21
 - With $W = 50$ m and $d = 5$ m, $r = 4.2$ m
- Step 4: Calculate the longitudinal diffusion coefficient (E)
- Use Figure 22
 - With $r = 4.2$ m and $U = 1$ m/s, $E = 69$ m²/s
- Step 5: Calculate alpha (α)
- Use Figure 23
 - With $E = 69$ m²/s and $t = 83$ min, $(\alpha) = 2000$
- Step 6: Calculate delta (Δ)
- Use Figure 24
 - With alpha (α) = 2000 and spill mass = 20 tonnes, delta (Δ) = 10
- Step 7: Compute the stream cross-sectional area (A)
- $A = W \times d = 50 \times 5 = 250$ m²
- Step 8: Calculate the maximum concentration (C) at the point of interest
- Use Figure 25
 - With $\Delta = 10$ and $A = 250$ m², $C = 40$ ppm

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of morpholine 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 26
 - With $r = 1000$ m, $d = 5$ m, the volume is approximately 1.5×10^7 m³

Step 3: Determine the average concentration

- . Use Figure 27
- . With $V = 1.5 \times 10^7 \text{ m}^3$ 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 soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of morpholine onto soil and its transport downward through the soil are presented here.

When morpholine is spilled onto soil, evaporation will occur to some degree, with the production of vapours which are denser than air. While some is lost to evaporation, the balance will infiltrate the soil. Evaporation will continue within the soil but at a reduced rate more closely related to that of water.

If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run-off and/or evaporate.

For this work, the soils have been assumed to be at field capacity (the maximum water a soil can hold after the excess is drained). This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

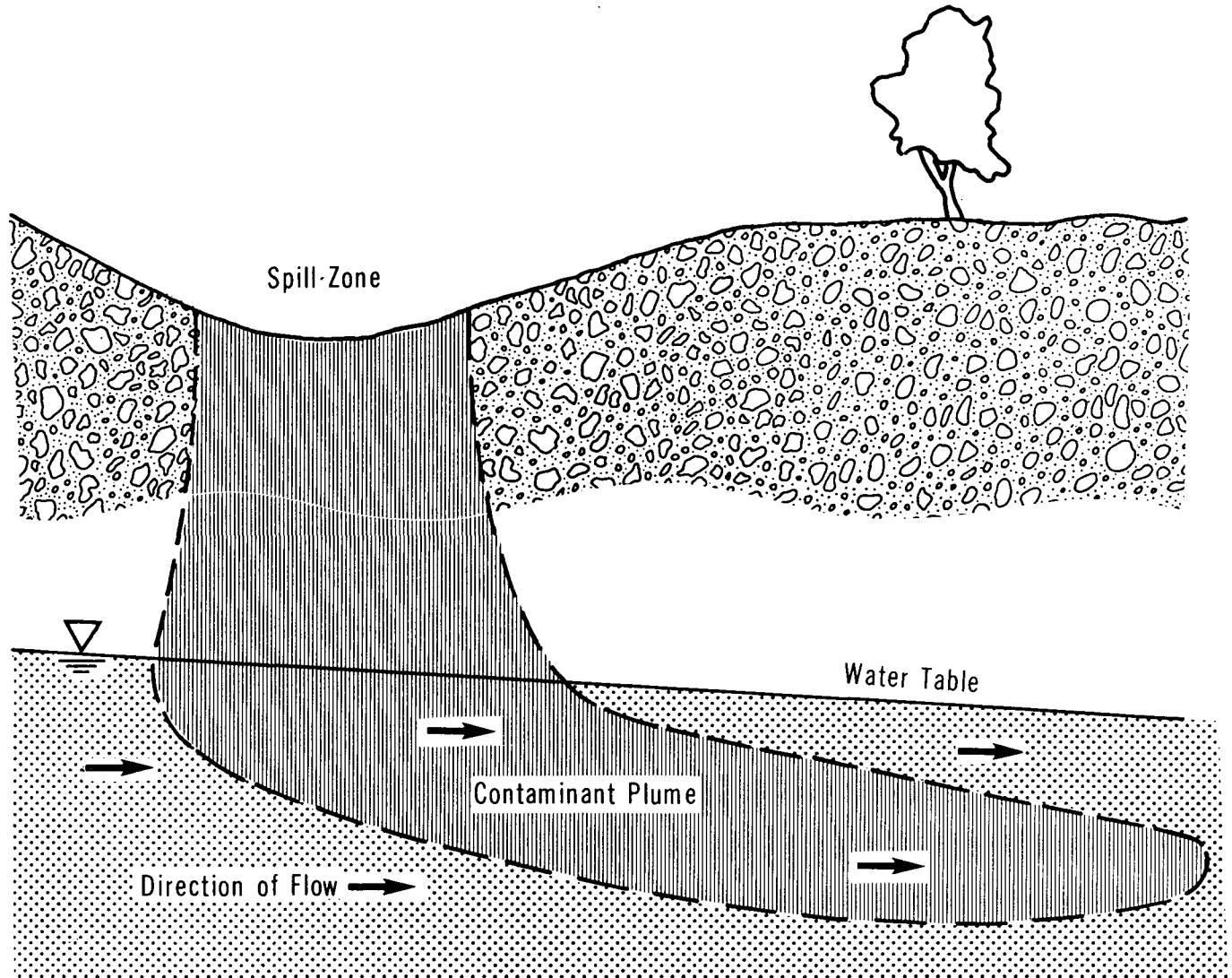
During transport through the soil, morpholine may be retarded through interactions such as adsorption onto soil surface. However, the extent to which this occurs is very difficult to predict. Consequently, the analysis used here neglects these retarding factors.

Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with diffusion serving to reduce the concentrations somewhat. This is shown schematically in Figure 28.

5.5.2 Equations Describing Morpholine Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

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SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m²

–Field Capacity (θ_{fc}) = 0.075

5.5.3 Saturated Hydraulic Conductivity of Morpholine in Soil. The saturated hydraulic conductivity, (K_0), in m/s, is given by:

$$K_0 = \frac{(\rho g)k}{\mu}$$

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

The fluids of interest are pure morpholine, morpholine diluted due to precipitation or mixture with groundwater, and water. Unfortunately, values of ρ and μ for pure morpholine were not obtained. Thus, only the diluted morpholine case, having ρ and μ essentially equal to those of water, has been presented.

Property	Diluted Morpholine (4°C)	Water (20°C)
Mass density (ρ), kg/m^3	1000	998
Absolute viscosity (μ), $Pa \cdot s$	1.57×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_0), m/s	$(0.62 \times 10^7)k$	$(0.98 \times 10^7)k$

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

Property	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 diluted morpholine into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p .

A flowchart for the use of the nomograms is presented in Figure 29. The nomograms are presented as Figures 30, 31 and 32. The water line on the nomograms represents the maximum penetration of water at 20°C in time t_p . It is a limiting condition as morpholine becomes diluted with water.

5.5.6 Sample Calculation. A 20 tonne spill of morpholine has occurred on silty sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 4 days after the spill.

Solution

Step 1: Define parameters

- Spill mass = 20 000 kg (20 tonnes)
- $T = 20^\circ\text{C}$
- $r = 8.6 \text{ m}$
- Soil = silty sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 4 d

Step 2: Calculate the area of the spill

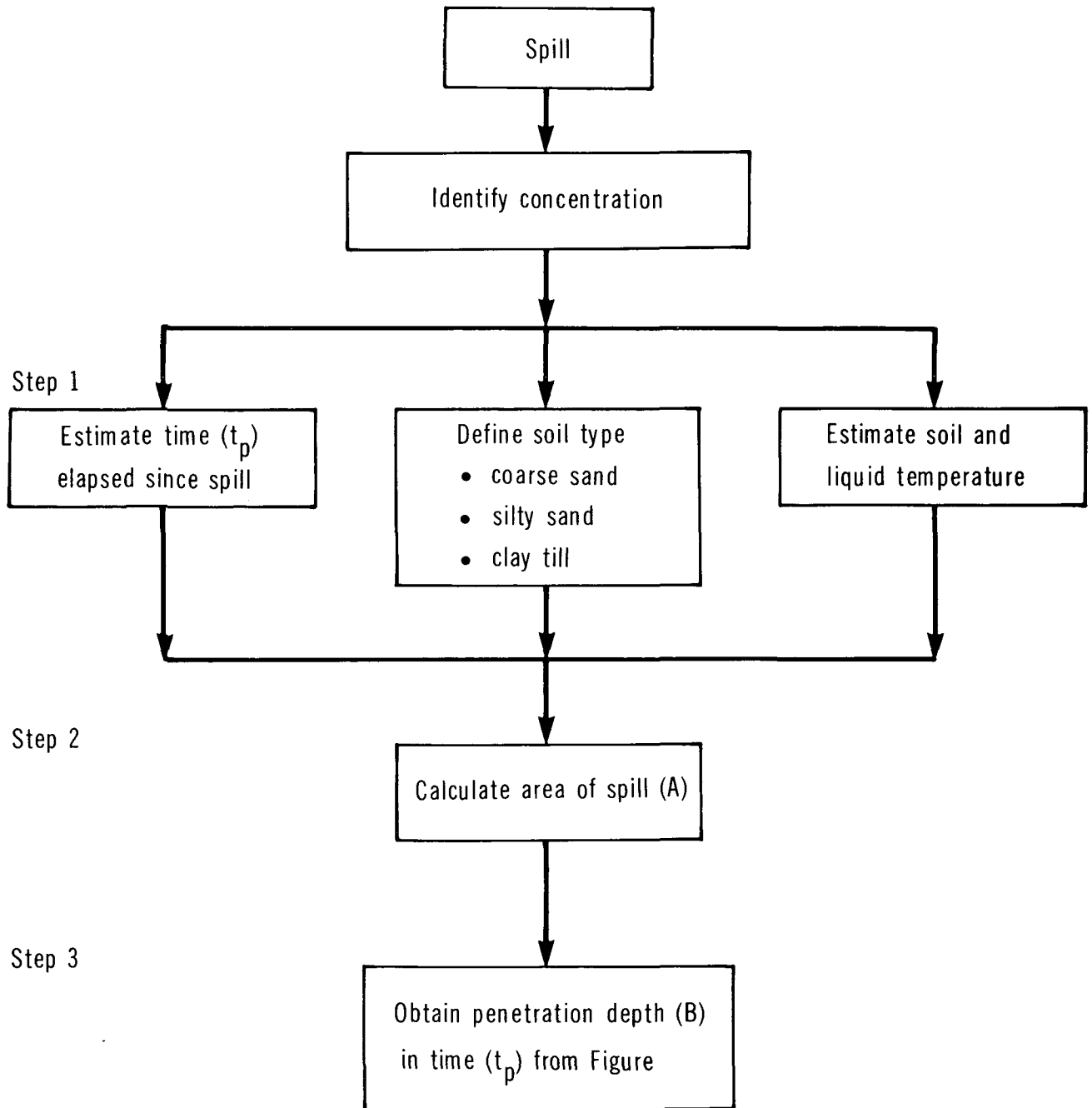
- $A = \pi r^2 = 232 \text{ m}^2$

Step 3: Estimate the depth of penetration (B) at time (t_p)

- For silty sand, $B = 3.5 \text{ m}$ at $t_p = 4 \text{ d}$
- Groundwater table has not been reached in this time

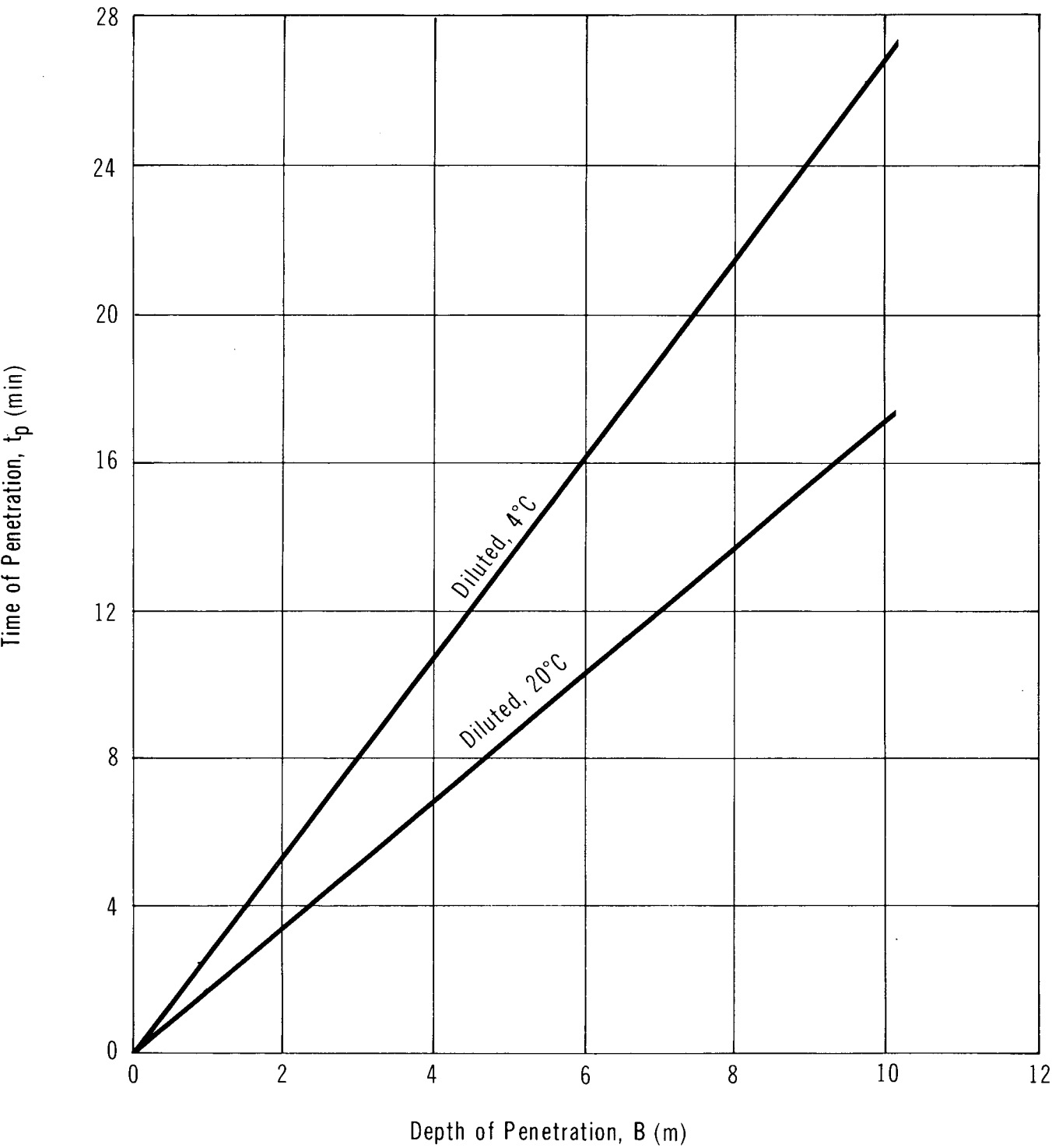
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FLOWCHART FOR NOMOGRAM USE



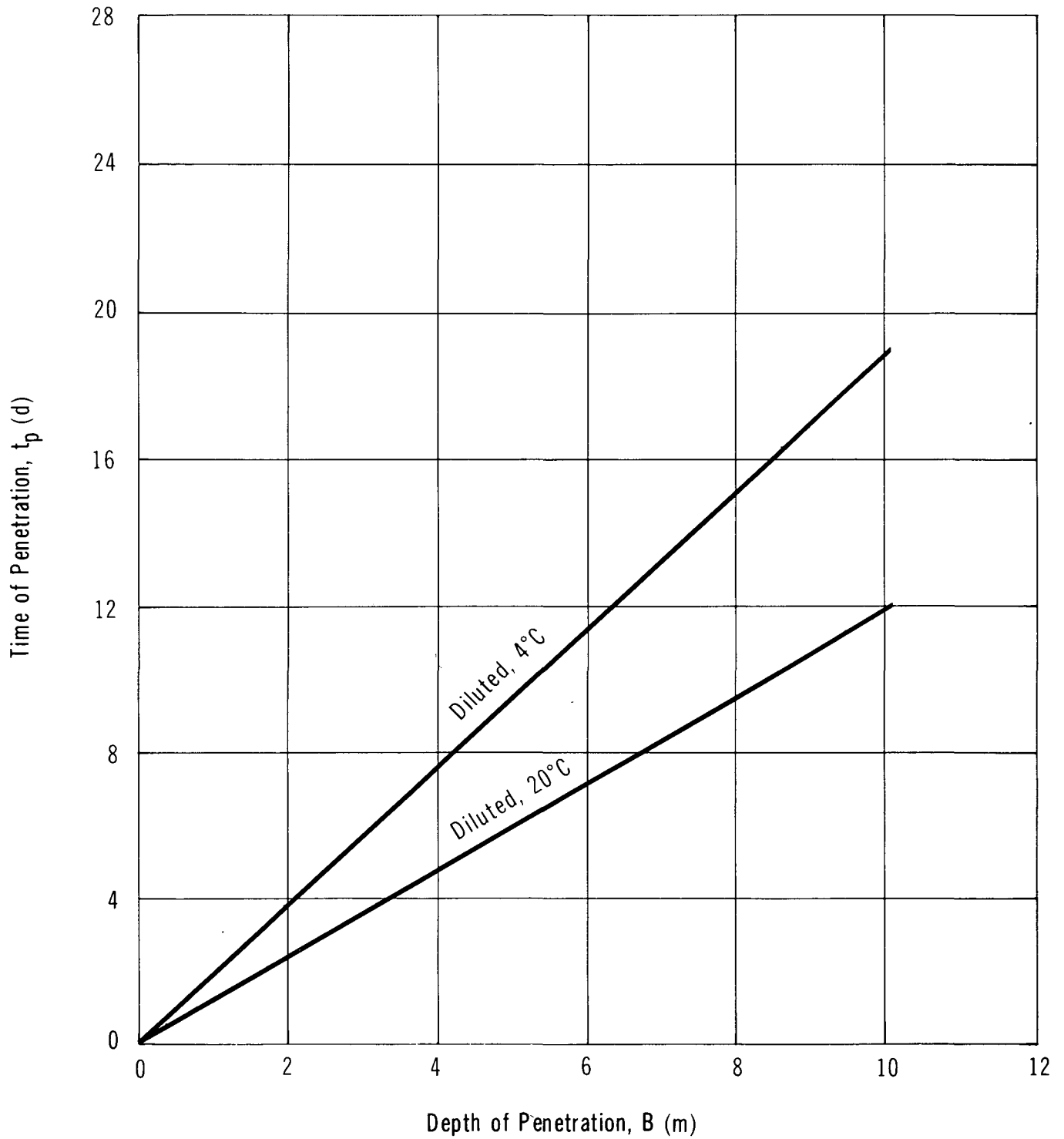
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PENETRATION IN COARSE SAND



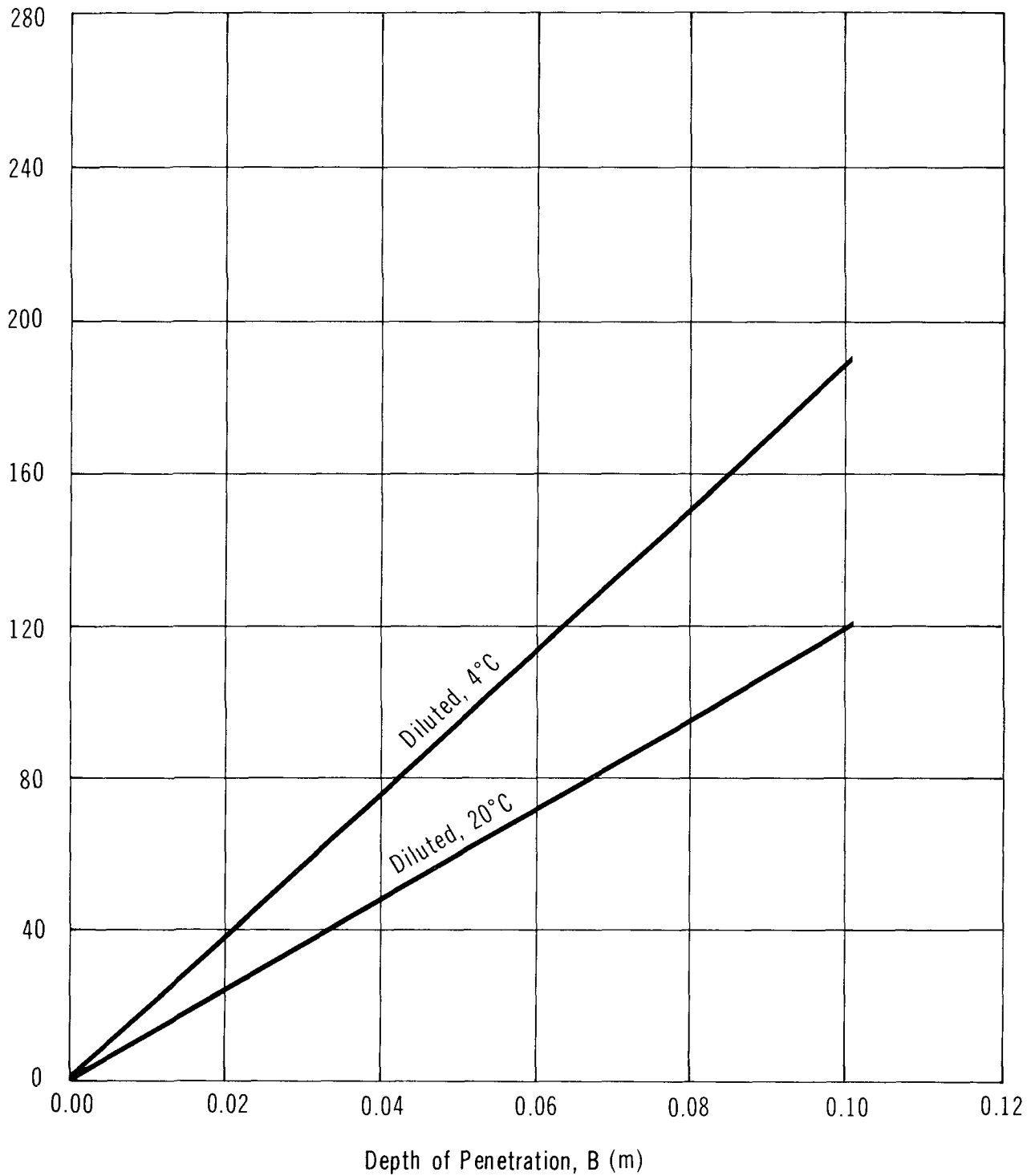
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PENETRATION IN SILTY SAND



MORPHOLINE

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 **Water.** No limits specified.

6.1.2 **Air.** No limits specified.

6.2 Aquatic Toxicity

6.2.1 **U.S. Toxicity Rating.** Morpholine has been assigned a TL_m96 of 100 to 1000 ppm (RTECS 1979).

6.2.2 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Toxicity Tests - Freshwater</u>					
119	24	<i>Daphnia magna</i>	LC ₅₀	static, 20°C	Calamari 1980
350	96	Bluegill	TL ₅₀	static, 23°C	U.S. Testing 1975
380	96	Rainbow trout	LC ₅₀	static, 20°C, soft (20 HD)	Calamari 1980
180	96	Rainbow trout	LC ₅₀	static, 20°C, hard (320 HD)	Calamari 1980
>1000	96	Zebra fish	LC ₅₀	-	WPCF 1983
240-285	96	Golden orfe	LC ₅₀	-	WPCF 1983
<u>Fish Toxicity Tests - Saltwater</u>					
400	96	Atlantic silverside	TL ₅₀	saltwater, static, 23°C	U.S. Testing 1975
<u>Microorganisms</u>					
4.1	-	Green algae (<i>Scenedesmus quadricauda</i>)	inhibition of cell multiplication	-	Verschueren 1984

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
310	-	Bacteria (<i>Pseudomonas putida</i>)	inhibition of cell multiplication	-	Verschuere 1984
28	96	Algae (<i>Selenastrum capricornutum</i>)	EC ₅₀ inhibition of 50 percent of growth	20°, static	Calamari 1980
1.7	-	Algae (<i>Microcystis aeruginosa</i>)	inhibition of cell multiplication	-	Verschuere 1984
12	-	Protozoa (<i>Entosiphon sulcatum</i>)	inhibition of cell multiplication	-	Verschuere 1984
815	-	Protozoa (<i>Uronema parduczi</i>)	inhibition of cell multiplication	-	Verschuere 1984

6.3 Mammalian Toxicology

Morpholine has been given an oral acute toxicity rating of 1000 to 2499 mg/kg, based on the LD₅₀ data in mammals (WQCDB-1 1970).

6.4 Effect Studies

Morpholine has been identified as an olfactory indicator of territory for fish. In one experiment, 18-month-old hatchery-raised fish were exposed to morpholine for 40 days. During spawning, a large number (18 percent vs 1 percent in controls) were captured at a simulated stream scented with morpholine (Scholz 1978). In another study, morpholine was used as an attractant in a secondary tributary devoid of anadromous salmonids. A number of trout and salmon entered the stream, leading to the conclusion that morpholine can act as a nonspecific attractant to nonimprinted fish (Mazeaud 1981). In a study to determine threshold levels, an electrophysical apparatus was used. This

study showed that there was no evidence that rainbow trout could detect morpholine at concentrations lower than 10^{-4} M or that imprintation could occur at levels of 5.7×10^{-10} M (Hara 1979).

6.5 Degradation

B.O.D. kg/kg	B.O.D. % Theor.	Days	Seed	Method	Reference
0.02	0.9	5	Standard dilute sewage	-	Verschueren 1984
>1	58	10	Nonflocculating growth		Gaufin 1965
<1	0.9	5	Sewage seed		Gloyna 1963
<1	5.1	20	Sewage seed		Gloyna 1963
<1	30	5			Mills 1955
>1	70	10			Mills 1955

In a respirator test, morpholine showed no fundamental degradation (Calamari 1980).

6.6 Environmental Sources

Morpholine is often used as a corrosion inhibitor in boilers. It is often found in steam or even in drinking water as a result of this use. In one study, sterilization steam in a hospital was found to contain an average of 2.4 mg/L morpholine; and steam in a food processing plant was found to contain an average of 1.1 mg/L morpholine (Amines 1979).

6.7 Long-term Fate and Effects

Morpholine biodegrades at a moderate rate. No bioaccumulation or food chain concentration has been cited (OHM-TADS 1981).

7 HUMAN HEALTH

Morpholine is a colourless, hygroscopic oil with an unpleasant, amine-like odour readily detectable at concentrations very much below the present recommended exposure standard (GE 1979). It is a secondary amine. Its health effects are similar to those of ammonia; however, the potential for systemic effects is greater in the case of morpholine exposure (Doc. TLV 1981). Liver and kidney damage has been reported in animal studies. Morpholine is readily absorbed through the intact skin. It is a skin and eye irritant in man although no chronic effects in man as a result of repeated exposure were found in the literature (Doc. TLV 1981).

No major toxicity review monographs were found in the literature. Morpholine has been tested for carcinogenicity, with inconclusive results (Patty 1981). No data were found on its potential as a mutagen or teratogen. The compound was reported in the EPA TSCA Inventory (RTECS 1979).

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. With the exception of data pertaining to mutagenicity, teratogenicity and carcinogenicity, only acute (short-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where applicable.

7.1 Recommended Exposure Limits

The exposure standards for morpholine are based upon its potential for systemic effects (in comparison with ammonia), and the standard has been deemed to be low enough to prevent irritation and harmful effects on the eyes and vision (Doc. TLV 1981). Canadian provincial guidelines generally are similar to those of the USA-ACGIH unless indicated otherwise.

Guideline	Origin	Recommended Level	Reference
<u>Time-weighted Averages (TWA)</u>			
TLV* (8 h) skin	USA-ACGIH	20 ppm ($\approx 70 \text{ mg/m}^3$)	TLV 1983
PEL (8 h)	USA-OSHA	20 ppm ($\approx 70 \text{ mg/m}^3$)	NIOSH/OSHA 1981

Guideline	Origin	Recommended Level	Reference
<u>Short-term Exposure Limits (STEL)</u>			
STEL (15 min)	USA-ACGIH	30 ppm ($\approx 105 \text{ mg/m}^3$)	TLV 1983
Ceiling (15 min)	USA-OSHA	30 ppm ($\approx 105 \text{ mg/m}^3$)	Patty 1981
<u>Other Human Toxicities</u>			
IDLH	USA-NIOSH	8000 ppm	NIOSH Guide 1978

Inhalation Toxicity Index

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

$$\text{ITI} = 1315.12 (\text{Vapour Pressure, in mm Hg/TLV}^\circ, \text{ in ppm})$$

At 20°C, ITI = 1315.12 (6.75 mm Hg/20 ppm)

At 20°C, ITI = 4.44×10^2

7.2 Irritation Data

7.2.1 Skin Contact. Morpholine can penetrate intact skin. Systemic effects as a result of skin exposure are reported in Section 7.4.4.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Some instances of skin irritation have been reported	Patty 1981
Unspecified	Morpholine is a primary skin irritant and induces hypersensitive responses. People with pre-existing skin disorders may be more susceptible to the effects of this agent	NIOSH/OSHA 1981
SPECIES: Rabbit		
995 mg (24 h)	Severe irritation	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
500 mg	Open skin test: moderate irritation	RTECS 1979
0.9 g/kg undiluted	Two out of seven animals died, severe penetrating burns	Patty 1981
0.5 g/kg (24 h) undiluted	LD ₅₀	Kirk-Othmer 1980
0.5 mL undiluted	Corrosive	Patty 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
"Low concentrations"	Have caused transient corneal edema and temporary fogging of vision with halos around lights in workers exposed for many hours. These symptoms appear after work and disappear by the next day	Patty 1981
Unspecified	Morpholine is an eye irritant and has caused corneal edema in workers	NIOSH/OSHA 1981
SPECIES: Rabbit		
0.1 mL undiluted	Irritation score = 67.7/110	Patty 1981
0.005 mL undiluted	Corneal injury	Patty 1981
40 percent mixture	Corneal injury	Patty 1981
2 mg	Severe irritation	RTECS 1979

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: Fishy, amine-like hedonic tone; unpleasant (Verschueren 1984).

Odour Index: 75 000 (Verschueren 1984).

Parameter	Media	Concentration	Reference
Odour Detection Threshold	In air	0.01 ppm	ASTM 1980
Odour Recognition Threshold	In air	0.07 ppm	ASTM 1980
100 Percent Recognition	In air	0.14 ppm	Verschueren 1984

7.3.2 Taste. No data.

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Human		
12 000 ppm (1 min)	Nose irritation	Doc. TLV 1981
12 000 ppm (1 1/2 min)	Coughing	Doc. TLV 1981
Unspecified	Transfer of morpholine by pipette caused a severe sore throat and reddened mucous membranes. These symptoms cleared on cessation of the experiment	Doc. TLV 1981
800 ppm	No visible effects for short exposures	Ullmann 1975
SPECIES: Rat		
Saturated vapour (4 h)	Death	Patty 1981
18 000 ppm (8 h)	Some deaths	Verschueren 1984
12 000 ppm (8 h)	No deaths. Reversible respiratory tract and systemic injury	Patty 1981
8000 ppm (8 h)	No deaths in 6 rats	Patty 1981
SPECIES: Guinea Pig		
120 000 ppm (8 h)	No deaths. Reversible respiratory tract and systemic injury	Patty 1981
SPECIES: Mouse		
1320 mg/m ³	LC ₅₀	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
SPECIES: Animal (unspecified)		
Unspecified	Nasal and bronchial irritation as with ammonia gas, and liver damage predominated	Doc. TLV 1981
<u>Chronic Exposures</u>		
SPECIES: Human		
Unspecified	At low concentrations, skin and eye irritation have been reported as well as respiratory tract irritation. No chronic effects have been reported	Patty 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Human		
Unspecified	Ingestion may cause digestive tract damage	GE 1979
3.8 g/kg	LD ₅₀	Kirk-Othmer 1978
SPECIES: Rat		
1.6 g/kg	LD ₅₀	Patty 1981
1.05 g/kg	LD ₅₀ , hypermia of lungs	Patty 1981
SPECIES: Guinea Pig		
0.9 g/kg	LD ₅₀	Patty 1981
SPECIES: Hamster		
0.05 g/kg	LD _{LO}	Patty 1981

7.4.3 Intraperitoneal.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Mouse		
0.413 g/kg	LD ₅₀	Patty 1981

7.4.4 Skin Contact. Morpholine can be absorbed through the intact skin. Only systemic effects as a result of skin exposure are reported in this section. See Section 7.2.1 for skin irritation data.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Rabbit		
1.21 g/kg	LD ₅₀ , hypermia of lungs and liver	Patty 1981
0.9 g/kg, 50 per- cent v/v aq.	Occlusive. Seven out of seven died before the 11th dose; skin burns, systemic injury	Patty 1981
0.5 mL/kg	LD ₅₀	Patty 1981

7.4.5 Mutagenicity, Teratogenicity and Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
1330 mg/kg (28 wk)	TD _{LO} , neoplasms (oral)	ITII 1981
Unspecified	Morpholine exposure in conjunction with N-nitroso-compounds. Morpholine alone did not induce lung tumours; however, other tissues were not studied	Patty 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rats		
Unspecified	Rats fed morpholine alone had a low number of tumours compared to a group fed nitrites and morpholine. The base-line controls had no tumours. May be weakly carcinogenic in rats	Patty 1981

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Irritation of the skin and eyes.
2. Respiratory tract irritation.
3. Coughing (Doc. TLV 1981).
4. Headache (CHRIS 1978).
5. Sore throat (Doc. TLV 1981).
6. Nausea (CHRIS 1978).
7. Difficult breathing (CHRIS 1978).

7.5.2 Ingestion.

1. Digestive tract damage (GE 1979).

7.5.3 Skin Contact.

1. Skin irritation.
2. Hypersensitive skin response (NIOSH/OSHA 1981).
3. Burns (CHRIS 1978).
4. The liquid is corrosive to tissue (GE 1979).
5. May be absorbed through the skin causing headache and nausea (CHRIS 1978).

7.5.4 Eye Contact.

1. Seeing halos around lights (Patty 1981).
2. Temporary fogging of vision (Patty 1981).
3. Irritation.
4. Transient corneal edema (Patty 1981).
5. Burns (CHRIS 1978).

7.6 Human Toxicity to Decay or Combustion Products

When heated to decomposition, morpholine emits highly toxic fumes of oxides of nitrogen (Sax 1981). Combustion products include oxides of nitrogen and carbon (GE 1979).

7.6.1 Nitric Oxide, Nitrogen Dioxide, Nitrogen Tetroxide, Carbon Monoxide and Carbon Dioxide. Nitric oxide is a colourless gas with a sharp, sweet odour. It combines with hemoglobin which is oxidized in the blood to methemoglobin, with resulting anoxia. Nitric oxide is only slightly irritating to the upper respiratory tract and eyes; dangerous amounts of fumes may therefore be inhaled before any discomfort is noticed (Sax 1968). In air, nitric oxide is oxidized to nitrogen dioxide which is four to five times as toxic as nitric oxide (Patty 1963). The TLV[®] for nitric oxide is 25 ppm (8 h - TWA) and 35 ppm (STEL) (TLV 1983).

At normal environmental temperatures, nitrogen dioxide and nitrogen tetroxide are always found together (proportion of NO₂ to N₂O₄ at 37.5°C is 3:7 (Sax 1968). At higher temperatures, the proportion of NO₂ increases. Mixtures are often referred to as "nitrogen dioxide", which is dark brown with a pungent, acrid odour. Nitrogen dioxide is mildly irritating to the eyes, nose and upper respiratory mucosa; therefore, dangerous amounts of fumes may be inhaled before any discomfort is noticed. Nitrogen oxide is slightly soluble in water, reacting in the presence of oxygen to form nitric and nitrous acids. These acids are formed deep in the respiratory system where they irritate the lungs, causing congestion of the throat and bronchi, and edema of the lungs. Symptoms of exposure include weakness, nausea, abdominal pain, cough, mucoid frothy sputum, accelerated heart action, severe cyanosis and convulsions. Excessive exposures will result in death from asphyxia.

Immediate symptoms may clear up breathing fresh air; however, the above symptoms may ensue in 6 to 24 hours. In fatal cases, death occurs within 8 to 48 hours

following exposure. The TLV[®] for NO₂ is 3 ppm (8 h - TWA), and 5 ppm (STEL) (TLV 1983). There is no TLV[®] for nitrogen tetroxide.

Carbon monoxide is a colourless, practically odourless gas which is a chemical asphyxiant. It causes hypoxia by complexing with hemoglobin and reducing the oxygen-carrying capacity of the blood. Excessive exposures will result in death from asphyxia. More moderate exposures may cause headaches and affect mental functions. The effects of moderate exposures are reversible, although considerable time is required to reverse the carbon monoxide-hemoglobin complexing reaction. The TLV[®] for carbon monoxide is 50 ppm (8 h - TWA) and 400 ppm (STEL) (TLV 1983).

Carbon dioxide is a colourless, odourless gas which in elevated concentrations may act to produce mild narcotic effects, respiratory stimulation, and asphyxiation. Its TLV[®] is 5000 ppm (8 h - TWA) and 15 000 ppm (STEL) (TLV 1983).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Morpholine with Other Chemicals and Chemical Groups

	SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF POLYMERIZATION	VIOLENT POLYMERIZATION	DECOMPOSITION OF FLAMMABLE GASES	FORMATION OF TOXIC FUMES	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
<u>GENERAL</u>														
Fire					•	•							May evolve highly toxic fumes of nitrogen oxides in fire area	Sax 1979; NFPA 1978
Heat		•		•	•								Flammable liquid. When heated to decomposition, highly toxic fumes of nitrogen oxides are evolved	Sax 1979; NFPA 1978
<u>SPECIFIC CHEMICALS</u>														
Cellulose Nitrate		•											Spontaneous ignition	Bretherick 1979
Nitromethane			•										Danger of explosion if initiated by detonation	Bretherick 1979

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

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION											SPECIFICS	REFERENCE
	FIRE	EXPLOSION	FORMATION OF VIOLENT POLYMERIZATION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION OF POLYMERIZATION	FORMATION OF TOXIC FUMES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION			
Alkali and Alkaline Earth Metals		•										Flammable hydro- gen gas may be produced	EPA 600/2- 80-076
Epoxides	•											Condensation and ring opening may occur, caus- ing possible polymerization	EPA 600/2- 80-076
Halogenated Organics	•												EPA 600/2- 80-076
Isocyanates	•									•		Uncontrollable reaction	EPA 600/2- 80-076
Organic Acids	•					•							Ashland MSDS 1978
Organic Peroxides	•				•							Possible polymer- ization with evolution of toxic fumes of nitrogen oxides	EPA 600/2- 80-076
Oxidizing Agents	•				•							Evolution of toxic fumes of nitrogen oxides	EPA 600/2- 80-076

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

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF VIOLENT POLYMERIZATION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION OF GREATER TOXICITY	FORMATION OF TOXIC FUMES	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Reducing Agents	•	•	•									Flammable hydrogen gas may be produced in turn cause a fire	EPA 600/2-80-076
Strong Alkalis	•				•								Ashland MSDS 1978
Toxic Metals							•					Will increase solubility of toxic metal compounds in water	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 source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Morpholine is a flammable liquid. Vapours may travel along surfaces to distant ignition sources and flash back (NFPA 1978; Ashland MSDS 1978). Containers may explode in heat of fire (ERG 1980).

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to prevent rupture (NFPA 1978; ERG 1980).

Small fires: Dry chemical, CO₂, water spray or foam (alcohol).

Large fires: Water spray, fog or foam.

Move containers from fire area if this can be done without risk. Stay away from tank ends. Do not get water inside containers (ERG 1980).

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (GE 1977). Water spray may be used to disperse the vapours and to protect men attempting to stop a leak (NFPA 1978). A fluorocarbon water foam can also be applied to the spill to diminish vapour and fire hazard (EPA 670/2-75-042). Cellosize, an absorbent material, has shown possible applicability for vapour suppression and/or containment of morpholine in spill situations (ICI 1982).

9.1.3.2 Spills on land. Contain if possible by forming mechanical barriers to prevent spreading (EPA 670/2-75-042) and pump as much material as possible to a salvage tank (Ashland MSDS 1978). The remaining liquid may be neutralized with vinegar, dilute acid, or sodium dihydrogen phosphate (EPA 670/2-75-042; CG-D-16-77). It may also be absorbed on sand or vermiculite (GE 1977; Ashland MSDS 1978).

9.1.3.3 Spills in water. Contain if possible by using natural barriers to limit spreading (EPA 670/2-75-042). Sodium dihydrogen phosphate is recommended as an in situ neutralizing agent to avoid overdosing (CG-D-16-77). Dilute acid or environmentally acceptable strong acid may be used as neutralizing agents. Sorbents such as activated carbon, Amberlite XAD or IRA 900 and Dowex 50WX8 may also be considered (CG-D-38-76).

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills in water. Activated carbon can be applied on the dissolved portion at 10 percent the spill amount over the region occupied by 10 mg/L or greater concentrations. Mechanical dredges or lifts can then be used to remove immobilized masses of pollutants and precipitates (EPA 670/2-75-042).

9.1.4.2 General. The following treatment processes have shown possible applicability for spill countermeasures.

Process	Percent Removal (TSA 1980)
Carbon Adsorption	100
Resin Adsorption	100

Morpholine can also be removed from contaminated water by using activated sludge (Metry 1980).

9.1.5 Disposal. Waste morpholine must never be discharged directly into sewers or surface waters. Waste morpholine may be burned in an approved incinerator with afterburner and scrubber to remove toxic nitrogen oxides (GE 1977).

9.1.6 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 morpholine:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent any possibility of repeated or prolonged skin contact with liquid morpholine and its solutions (NIOSH/OSHA 1981).

- Styrene-butadiene rubber has a penetration time of greater than 1 hour. The following clothing materials show penetration times of about 1 hour: butyl rubber, nitrile coated with PVC, polyvinyl alcohol, PVC and Viton (Little 1983).
- Neoprene or butyl rubber is recommended for gloves (GE 1977).
- Butyl has been recommended as a chemical suit material (good resistance) for protection against morpholine (EE-20).
- Any clothing which becomes wet or contaminated with liquid morpholine should be removed immediately and not reworn until the morpholine is removed from the clothing (NIOSH/OSHA 1981).
- Eye wash stations and chemical safety showers should be readily available in areas of use and spill situations (GE 1977).
- The following is a list of the minimum respiratory protection recommended for personnel working in areas where morpholine is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required above 20 ppm
Vapour Concentration	
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
8000 ppm or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 8000 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.

Condition	Minimum Respiratory Protection* Required above 20 ppm
Escape	Any gas mask providing protection against organic vapours. Any escape self-contained breathing apparatus.

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

9.1.7 Storage Precautions. Store in a well ventilated, fire-proof solvent storage area. No smoking or open flames in areas of storage or use. Electrically interconnect and ground containers when transferring morpholine. Use nonsparking tools (GE 1977).

Avoid contact with strong oxidizing agents, strong alkalis and strong acids. Containers of this material may be hazardous when emptied (Ashland MSDS 1978).

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the 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 useful information.

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 Method for the Detection of Morpholine in Air

11.1.1 Gas Chromatography (NIOSH 1977). A range of 28.5 to 108.4 mg/m³ (5.4 to 20.6 ppm) of morpholine in air may be determined by gas chromatography using flame ionization detection.

A known volume of air is drawn through a 7 cm x 6 mm O.D. glass tube containing two sections of 20/40 mesh silica gel separated by a 2 mm portion of urethane foam. The front section contains 150 mg, whereas the back-up section contains 75 mg. A sample size of 20 L at 200 mL/min is recommended.

The sample tube is scored with a file in front of the first silica gel section and broken. The first section is transferred to a 2 mL stoppered sample container containing 1.0 mL of 0.05 M sulphuric acid. The sample is allowed to desorb for 30 min. A 0.5 mL aliquot of the desorbed sample is transferred to a clean vial and 50 µL of 1.2 M sodium hydroxide is added. The pH of the resulting solution should be >10. A 5 µL aliquot of sample is injected into a gas chromatograph equipped with a flame ionization detector. The back-up section is analyzed in a similar manner to determine if the quantity exceeds the capacity of the first section.

The morpholine is determined using a suitable electronic integrator which measures peak area in conjunction with a standard curve.

Typical gas chromatograph conditions are: nitrogen carrier gas flow at 50 mL/min, hydrogen gas flow at 65 mL/min, air flow at 500 mL/min, injector temperature at 250°C, detector temperature at 280°C, a column temperature of 200°C, and a 4 ft. by 1/4 in. stainless steel column packed with 80/100 mesh Chromosorb 103 which has a 3 in. Ascarite precolumn inserted at its inlet.

11.2 Qualitative Method for the Detection of Morpholine in Air

A range of 2 to 30 ppm of morpholine in air may be determined using a Gastec detector tube for morpholine. A known volume of air is drawn through a Gastec detector tube for morpholine using a Gastec detector tube pump. A colour change from pink to yellow indicates morpholine. The colour change is based on the reaction of morpholine with sulphuric acid, measured with a thymol blue indicator (Gastec).

11.3 Quantitative Method for the Detection of Morpholine in Water

11.3.1 Colorimetric (ASTM 1979). A range of 1 to 5 ppm of morpholine in water may be determined colorimetrically. Higher concentrations may be determined by sample dilution.

A minimum volume of 2 L of representative sample is collected in a suitable glass container having a polyethylene lined cap. A 100 mL volume of sample is transferred to an 227 mL bottle having a polyethylene lined cap. A 1 drop volume of 37 percent formaldehyde is added and the sample shaken for 15 s. A 5 mL volume of saturated sodium borate solution is added followed by two drops of carbon disulphide. The sodium borate solution is prepared by dissolving 40 g of sodium borate decahydrate in 1 L of water and adjusting the pH to 9.5 with 0.5 N sodium hydroxide.

A 1 mL volume of copper sulphate (2.0 g/L) is added to the sample, the sample shaken, and 1 drop of Triton X-100 added. The solution is shaken for 4 min and transferred to a 125 mL separatory funnel. The sample is allowed to stand for 1 min, shaken for 15 s, allowed to stand for 1 min. The sample is drawn off and the absorbance read on a suitable spectrophotometer at 430 nm using 1 cm matched cells. The morpholine is determined using a calibration curve.

11.4 Qualitative Method for the Detection of Morpholine in Water

A 100 mL sample is placed in a beaker. A 1 drop volume of 37 percent formaldehyde is added and the mixture shaken for 15 s. A 5 mL volume of sodium borate (40 g/L) is added followed by 2 drops of carbon disulphide. The sample is then shaken for 15 min. A 1 mL volume of copper sulphate solution (2.0 g/L) is added, the mixture shaken, the mixture allowed to stand for 1 min, then 1 drop of Triton X-100 is added. The mixture is shaken and transferred to a 125 mL separatory funnel, allowed to stand for 1 min, shaken for 15 s, then let stand for 1 min. The formation of a brown complex indicates morpholine (ASTM 1979).

11.5 Quantitative Method for the Detection of Morpholine in Soil

11.5.1 Partition Infrared (AWWA 1981). Concentrations greater than 40 ppm of morpholine may be determined using partition infrared spectrophotometry.

Approximately 20 g of soil, accurately weighed, are collected in a glass jar and dried by the addition of magnesium sulphate. Freon 113[®] (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the morpholine. Three extractions using 30 mL Freon[®] each time are carried out. The extracts are combined in a 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon[®]. The sample is scanned on a suitable infrared spectrophotometer from 3200 cm⁻¹ to 2700 cm⁻¹ using 1 cm matched cells. The sample concentration is determined from a calibration curve.

11.6 Qualitative Method for the Detection of Morpholine in Soil

The sample is collected and extracted as in Section 11.5.1. The sample is scanned on a suitable infrared spectrophotometer from 3200 cm⁻¹ to 2700 cm⁻¹ using 1 cm matched cells. The presence of characteristic absorption bands indicates morpholine (AWWA 1981).

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EnviroTIPS
Common Abbreviations

BOD	biological oxygen demand	°Be	degrees Baumé (density)
b.p.	boiling point	MMAD	mass median aerodynamic diameter
CC	closed cup	MMD	mass median diameter
cm	centimetre	m.p.	melting point
CMD	count median diameter	MW	molecular weight
COD	chemical oxygen demand	N	newton
conc	concentration	NAS	National Academy of Sciences
c.t.	critical temperature	NFPA	National Fire Protection Association
eV	electron volt	NIOSH	National Institute for Occupational Safety and Health
g	gram		
ha	hectare	nm	nanometre
Hg	mercury	o	ortho
IDLH	immediately dangerous to life and health	OC	open cup
Imp. gal.	imperial gallon	p	para
in.	inch	P _c	critical pressure
J	joule	PEL	permissible exposure level
kg	kilogram	pH	measure of acidity/alkalinity
kJ	kilojoule	ppb	parts per billion
km	kilometre	ppm	parts per million
kPa	kilopascal	P _s	standard pressure
kt	kilotonne	psi	pounds per square inch
L	litre	s	second
lb.	pound	STEL	short-term exposure limit
LC ₅₀	lethal concentration fifty	STIL	short-term inhalation limit
LC _{LO}	lethal concentration low	T _c	critical temperature
LD ₅₀	lethal dose fifty	TC _{LO}	toxic concentration low
LD _{LO}	lethal dose low	T _d	decomposition temperature
LEL	lower explosive limit	TD _{LO}	toxic dose low
LFL	lower flammability limit	TL _m	median tolerance limit
m	metre	TLV	Threshold Limit Value
m	meta	T _s	standard temperature
M	molar	TWA	time weighted average
MAC	maximum acceptable concentration	UEL	upper explosive limit
max	maximum	UFL	upper flammability limit
mg	milligram	VMD	volume mean diameter
MIC	maximum immission concentration	v/v	volume per volume
min	minute or minimum	w/w	weight per weight
mm	millimetre		
µg	microgram		
µm	micrometre		