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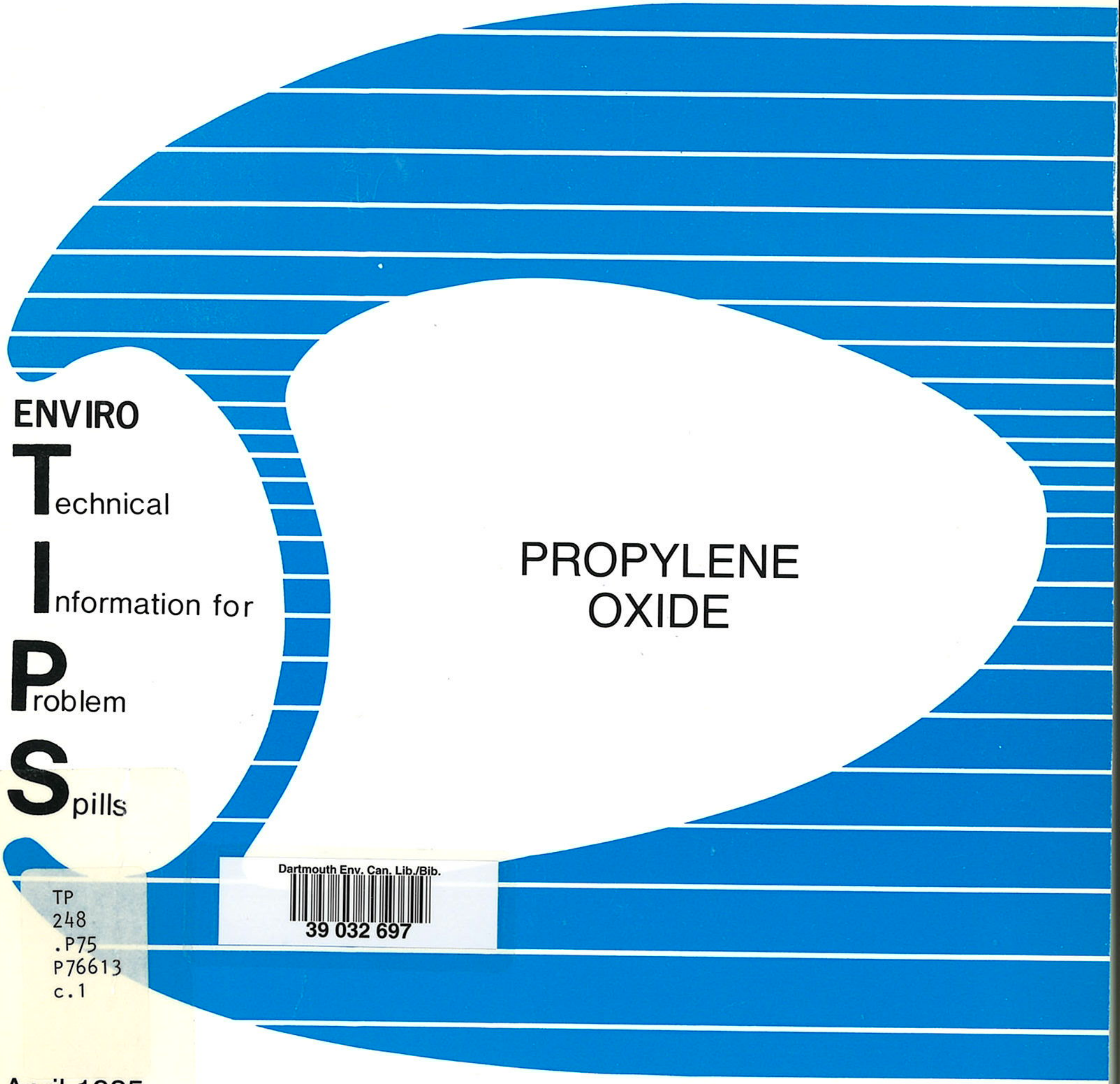

ENVIRO

Technical
Information for
Problem
Spills

PROPYLENE OXIDE

April 1985

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

The 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 report has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not 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.

EnviroTIPS manuals are available from:

Publications Section
Environmental Protection Service
Environment Canada
Ottawa, Ontario
CANADA
K1A 1C8

PROPYLENE OXIDE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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

April 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 Canadian Chemical Producers' Association is especially acknowledged for its review of and input to this manual. 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

PROPYLENE OXIDE (CH_3CHOCH_2)

Colourless liquid with a sweet, ether-like odour.

SYNONYMS

Epoxypropane; 1,2-Epoxypropane; Methyl Ethylene Oxide; Methyloxirane; Propene Oxide; 1,2-Propylene Oxide; Oxyde de Propylène (Fr.)

IDENTIFICATION NUMBERS

UN No. 1280; CAS No. 75-56-9; OHM-TADS No. 7216878; STCC No. 4906620

GRADES & PURITIES

Technical, 99.9 percent

IMMEDIATE CONCERNS

Fire: Flammable. Flashback along vapour trail may occur.

Human Health: Moderately toxic by inhalation.

Environment: Moderately toxic to aquatic life.

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): liquid
Boiling Point: 34.2°C
Melting Point: -112°C
Flammability: flammable
Flash Point: -37°C (CC)
Vapour Pressure: 58.6 kPa (20°C)
Density: 0.83 g/mL (20°C)

Solubility (in water): 40.5 g/100 g (20°C)
Behaviour (in water): mixes with no reaction
Behaviour (in air): vapour is heavier than air
Odour Threshold: 10 to 200 ppm

ENVIRONMENTAL CONCERNS

Propylene oxide is toxic to aquatic life at levels as low as 140 mg/L. As it evaporates quickly, propylene oxide does not persist long in soil or water.

HUMAN HEALTH

TLV®: 20 ppm (50 mg/m^3)
IDLH: 2000 ppm

Exposure Effects

Inhalation: Irritation to nose, throat and lungs, headache, nausea, and possible loss of consciousness

Contact: Contact with the skin causes irritation, burns and blisters. Contact with the eyes causes irritation and corneal burns.

Ingestion: Irritation and burns to the mouth and gastrointestinal tract, nausea and vomiting.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "FLAMMABLE". Call fire department and notify manufacturer. 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

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

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill. Remove spill with pumps or vacuum equipment, if possible. Absorb residual amounts of spill with noncombustible sorbents, and place into covered steel containers.

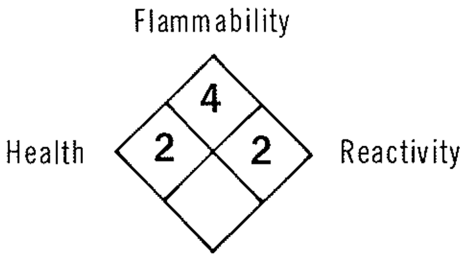
Water: Treat contaminated water, if possible.

Air: Use water spray to knock down and disperse flammable vapour. Control runoff for later treatment, if possible.

NAS HAZARD RATING

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

NFPA
HAZARD
CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Colourless liquid (Arco MSDS 1981)
Usual shipping state	Liquid
Physical state at 15°C, 1 atm	Liquid
Melting point	-112°C (Kirk-Othmer 1982; Ullmann 1975)
Boiling point	34.2°C (Kirk-Othmer 1982; Ullmann 1975)
Vapour pressure	58.6 kPa (20°C) (Kirk-Othmer 1982)

Densities

Density	0.83 g/mL (20°C) (Kirk-Othmer 1982)
Specific gravity	0.85 (0°C) (Arco MSDS 1981) 0.826 (25°/25°C) (Dow ERIS 1981)
Vapour density	2.0 (Arco MSDS 1981)

Fire Properties

Flammability	Flammable liquid (NFPA 1978)
Flash point, CC	-37°C (NFPA 1978)
Autoignition temperature	449°C (NFPA 1978)
Burning rate	3.3 mm/min (CHRIS 1978)
Upper flammability limit	37.0 percent (v/v) (NFPA 1978)
Lower flammability limit	2.8 percent (v/v) (NFPA 1978) 2.3 percent (v/v) (Ullmann 1975)
Heat of combustion	1750 kJ/mole (CHRIS 1978) 1890 kJ/mole (Ullmann 1975)
Combustion products	Carbon dioxide and water
Flashback potential	Vapour may travel considerable distance to a source of ignition and flash back (NFPA 1978)
Explosiveness	Vapours form explosive mixtures with air (NFPA 1978)
Behaviour in a fire	May polymerize with evolution of heat on contact with aluminum, etc.; may rupture container (NFPA 1978)
Electrical ignition hazard	May be ignited by static discharge

Other Properties

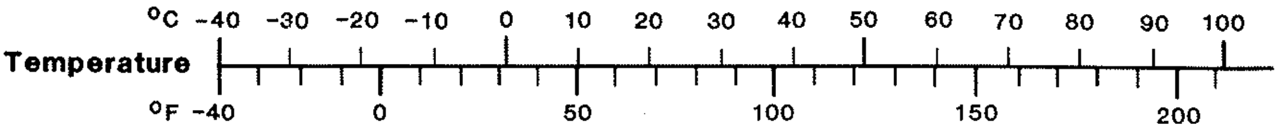
Molecular weight of pure substance	58.08 (CRC 1980)
Constituent components of typical commercial grade	99.9 percent propylene oxide (Dow MSDS 1980)
Refractive index	1.3670 (20°C) (CRC 1980)
Viscosity	0.327 mPa·s (20°C) (Lange's Handbook 1979)
Liquid interfacial tension with air	24.5 mN/m (15°C) (CHRIS 1978) 24.0 mN/m (20°C) (Ullmann 1975)
Latent heat of fusion	6.53 kJ/mole (at melting point) (Lange's Handbook 1979; Kirk-Othmer 1978)
Latent heat of sublimation	27.9 kJ/mole (25°C) (Lange's Handbook 1979)
Latent heat of vaporization	30.5 kJ/mole (at boiling point) (CRC 1980)
Heat of formation	Liquid: -122.6 kJ/mole (25°C) (Cox 1970) Gas: -94.7 kJ/mole (25°C) (Cox 1970)
Ionization potential	10.22 eV (Rosenstock 1977)
Heat of solution	-2.67 kJ/mole (CHRIS 1978)
Heat capacity (of vapour) constant pressure (C_p) constant volume (C_v)	 73 J/(mole·°C) (27°C) (CRC 1980) 64 J/(mole·°C) (27°C) (CRC 1980; CHRIS 1978)
Heat capacity (of liquid) constant pressure (C_p)	119.6 J/(mole·°C) (20°C) (Kirk-Othmer 1982)
Critical pressure	4924 kPa (CRC 1980; Kirk-Othmer 1982)
Critical temperature	209°C (CRC 1980; Kirk-Othmer 1982)
Saturation concentration	1280 g/m^3 (18°C) (calc.)
Dipole moment	1.98 D (Kirk-Othmer 1982)
Thermal conductivity	0.14 W/(m·K) (liquid at 20°C), 0.011 W/(m·K) (vapour at 25°C) (Kirk-Othmer 1982)
Coefficient of thermal expansion	0.00151/K (20°C, cubic) (Ullmann 1975)
Evaporation rate	11.5 g/(m^2·s) (this work)

Solubility

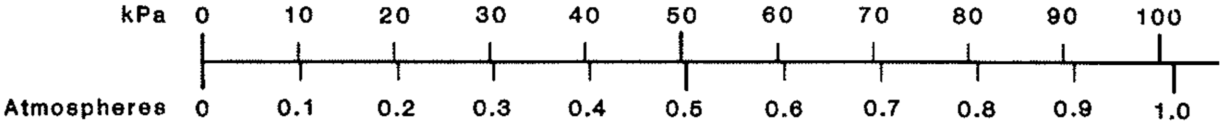
In water	40.5 g/100 g (20°C) (Dow ERIS 1981) 65 g/100 mL (30°C) (Verschueren 1984)
In other common materials	Miscible in ethanol and diethyl ether (CRC 1980)

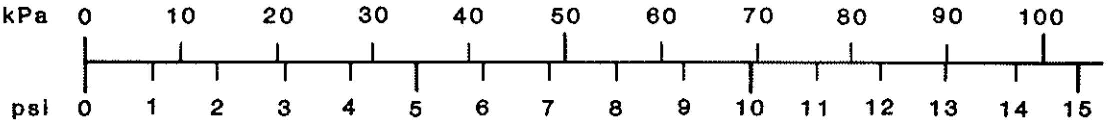
Vapour Weight to Volume Conversion Factor	1 ppm = 2.37 mg/m^3 (20°C) (Verschueren 1984)

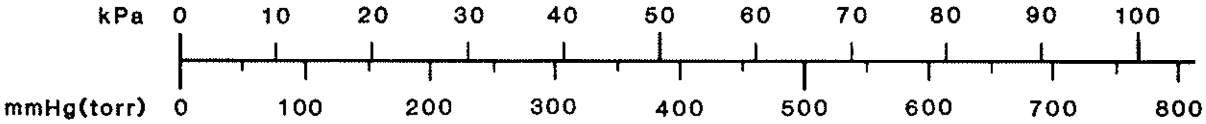
CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa







Viscosity

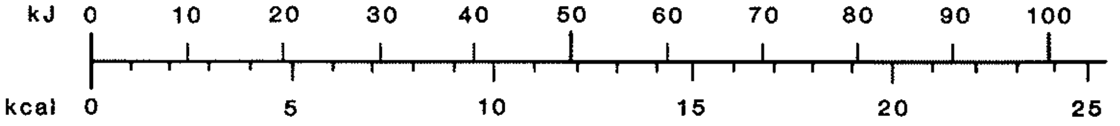
Dynamic 1 Pa·s = 1 000 centipoise (cP)

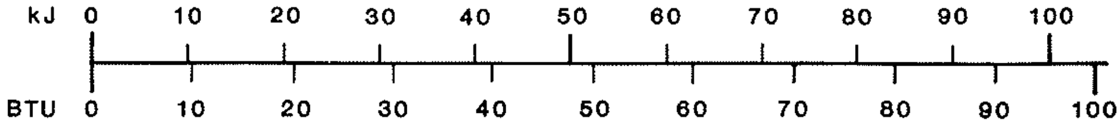
Kinematic 1 m²/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J





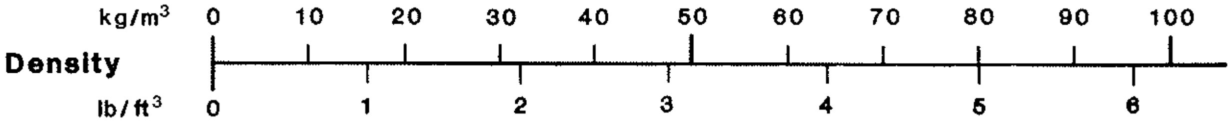


FIGURE 1

PROPYLENE OXIDE

VAPOUR PRESSURE vs TEMPERATURE

Reference: Chem. Eng. 1976

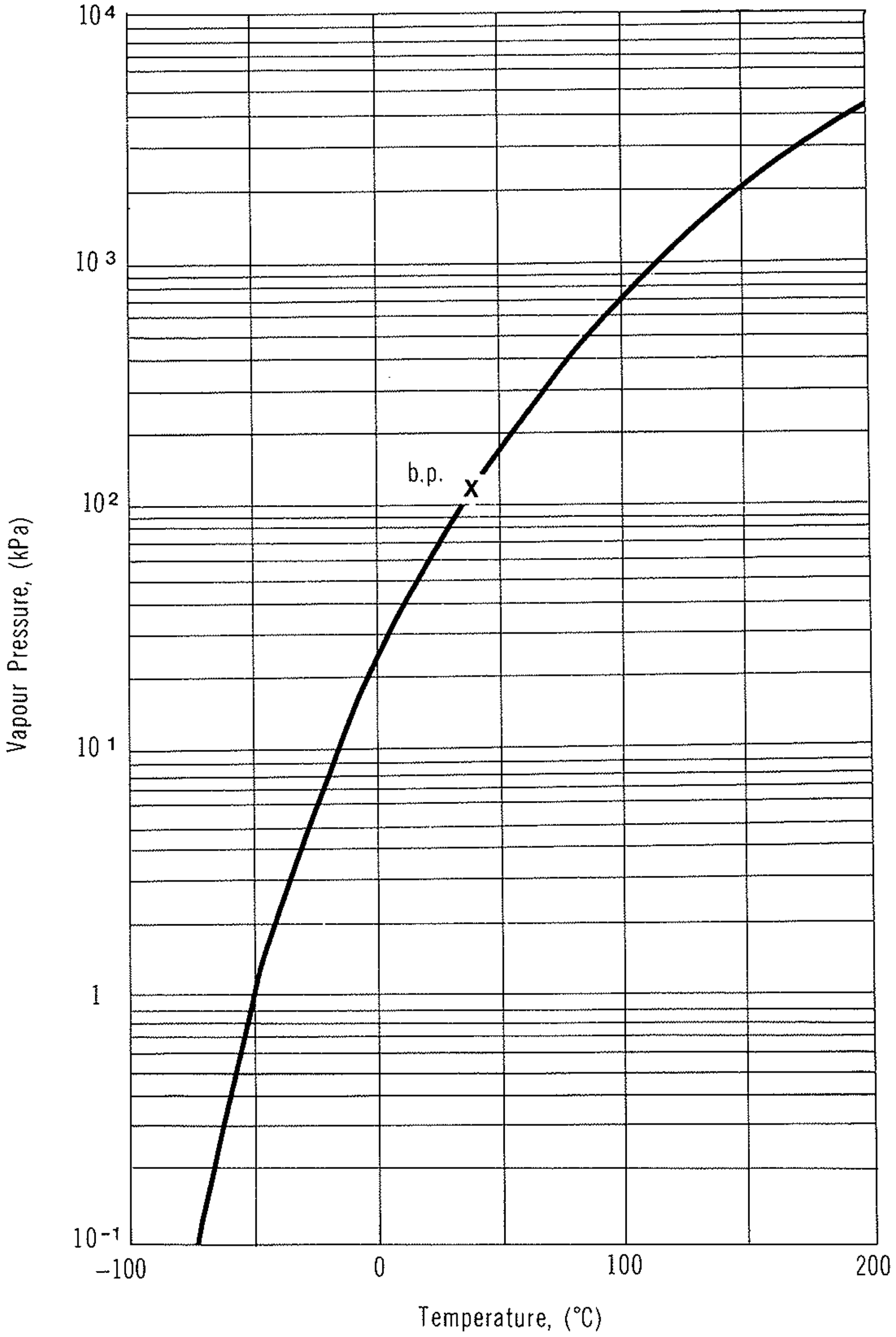


FIGURE 2

PROPYLENE OXIDE

LIQUID DENSITY VS TEMPERATURE

Reference: Chem.Eng.1976

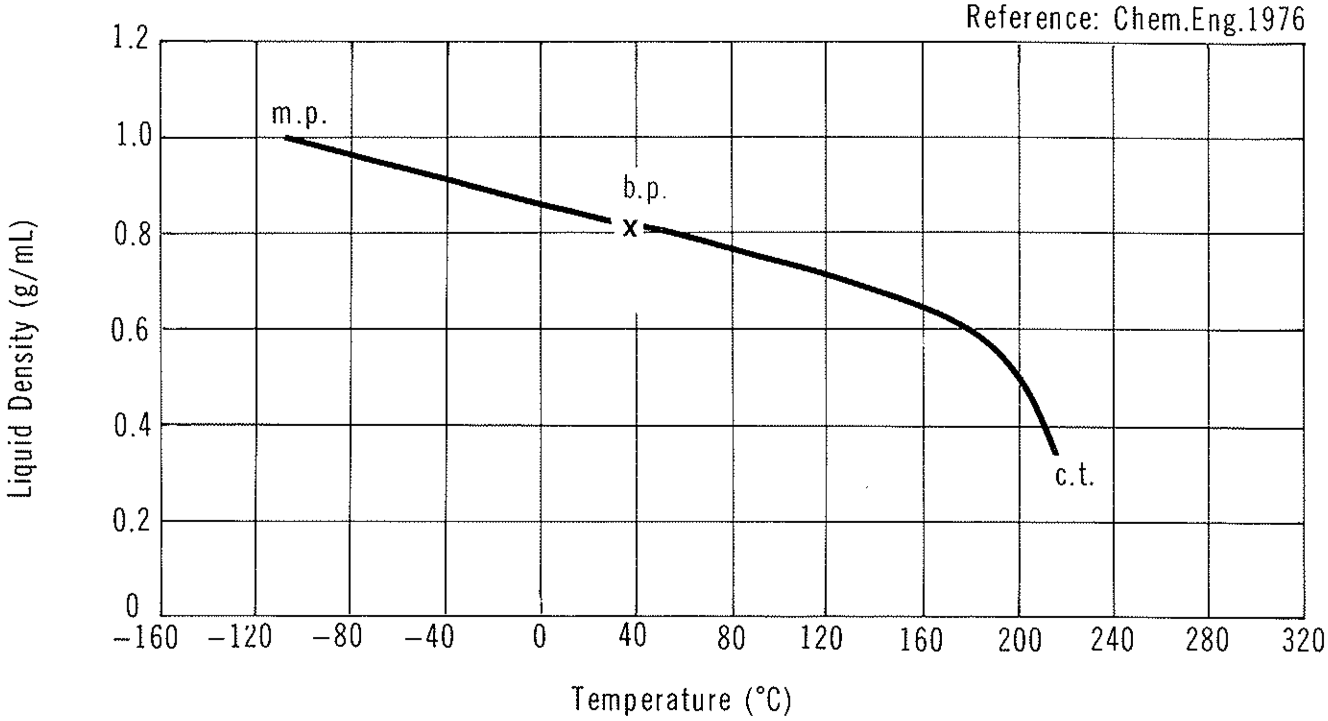


FIGURE 3

PROPYLENE OXIDE

PHASE DIAGRAM OF THE $C_3H_6O•H_2O$ SYSTEM

Reference: KIRK-OTHMER 1982; PPH 1974

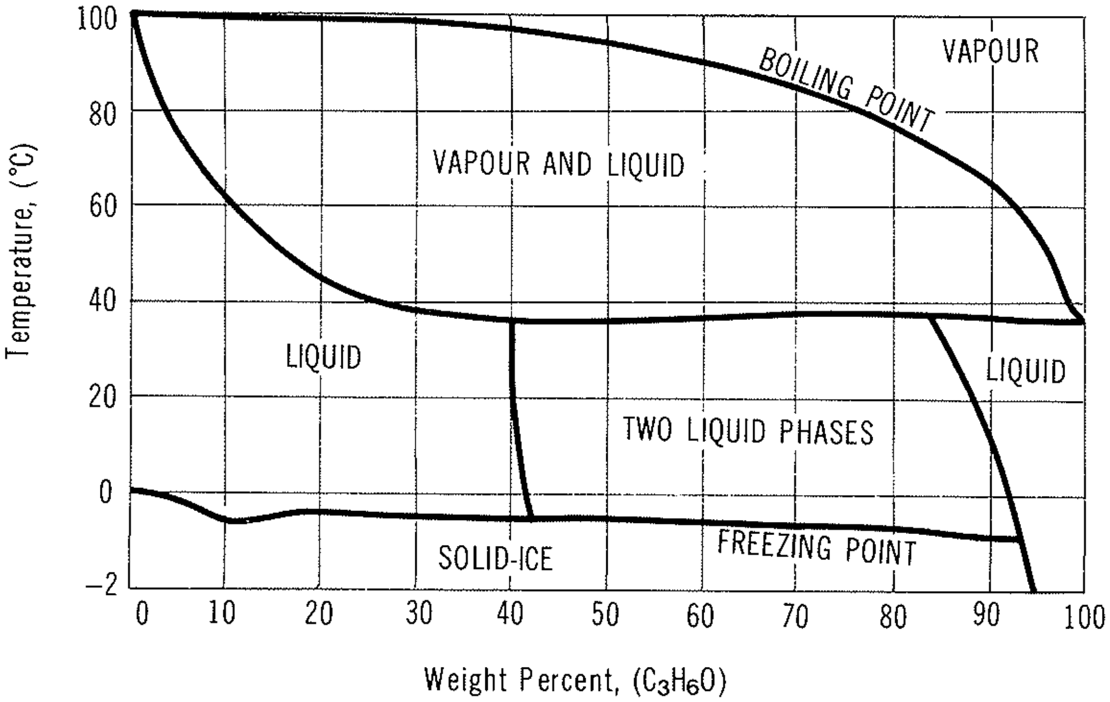


FIGURE 4

PROPYLENE OXIDE

VAPOUR VISCOSITY VS TEMPERATURE

Reference: Chem.Eng. 1976

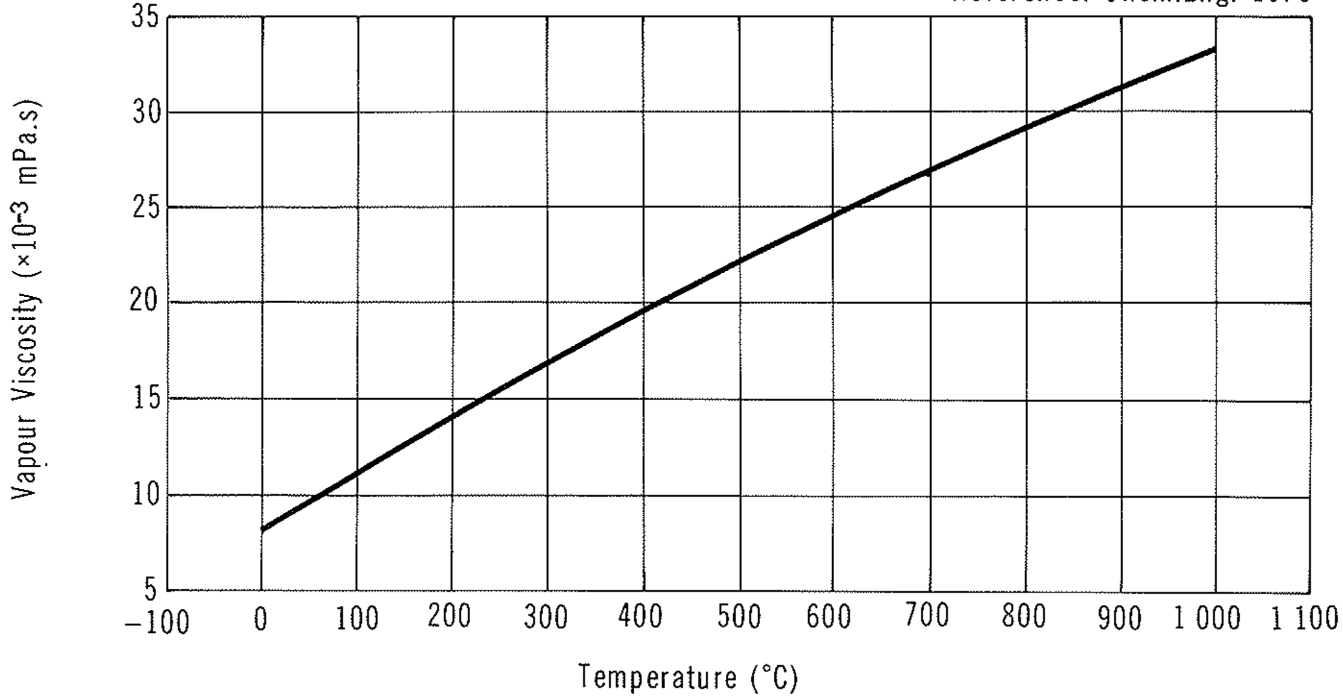


FIGURE 5

PROPYLENE OXIDE

LIQUID VISCOSITY VS TEMPERATURE

Reference: Chem.Eng. 1976

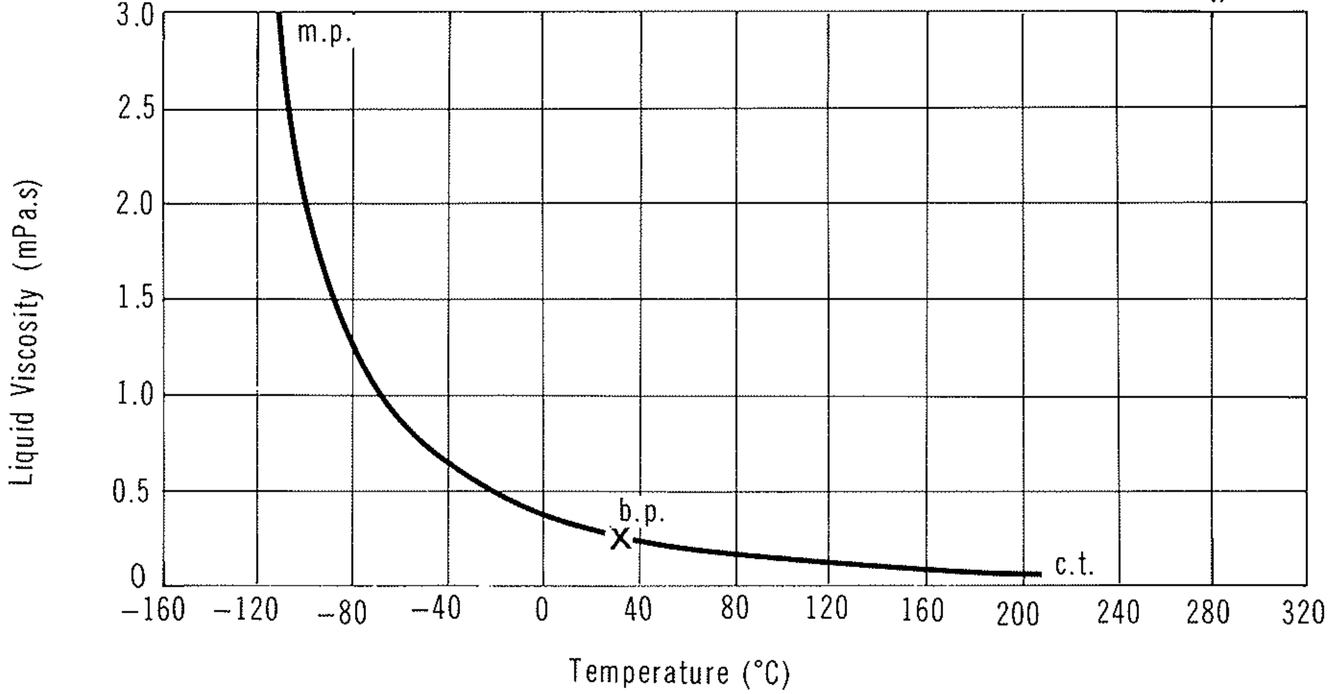
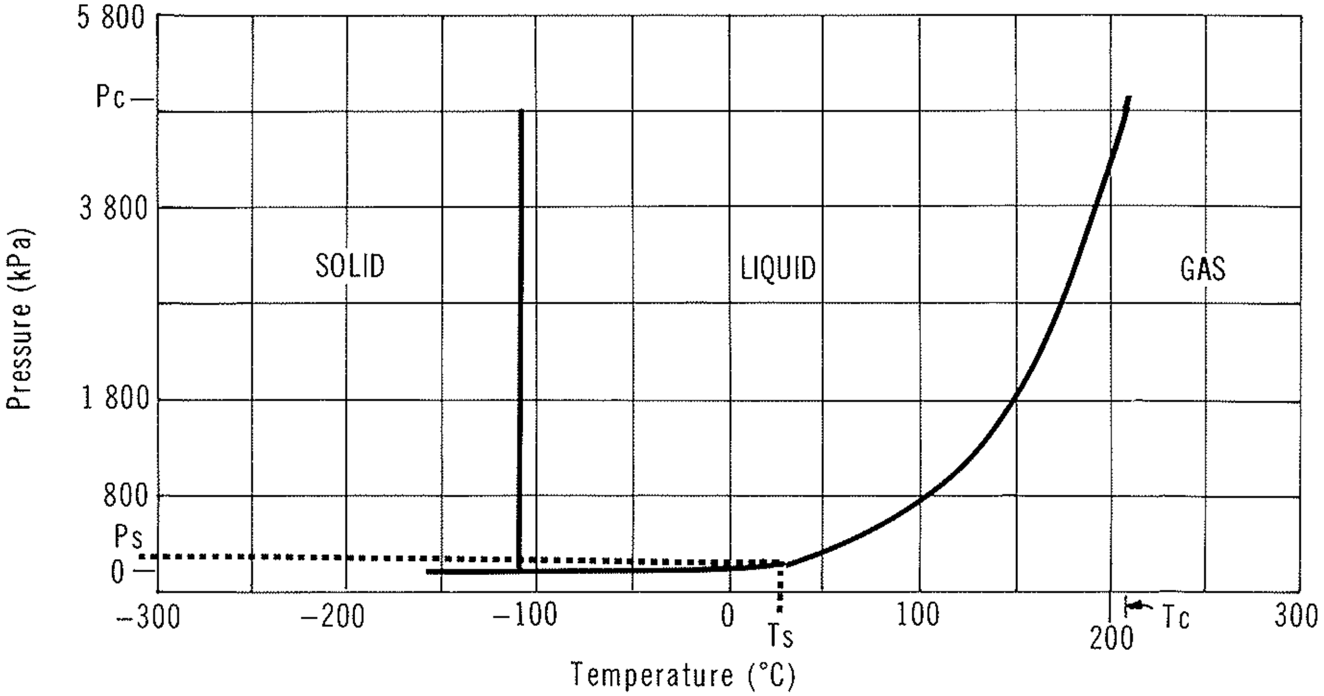


FIGURE 6

PROPYLENE OXIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Dow ERIS 1981)

Propylene oxide is sold in a technical grade with a minimum purity of 99.9 percent.

3.2 Domestic Manufacturer (Corpus 1983)

Dow Chemical Canada Inc.
Box 1012, Modeland Road
Sarnia, Ontario
N7T 7K7
(519) 339-3131

3.3 Other Supplier (CCPA 1984)

Texaco Chemicals Canada
250 Lakeshore Road West (Port Credit)
Mississauga, Ontario
L5G 4M6
(416) 278-5511

3.4 Major Transportation Routes

Current Canadian production of propylene oxide is in Sarnia, Ontario. Shipment is primarily by rail car to the United States, with some material being transported to southern Ontario and Quebec.

3.5 Production Levels (Corpus 1983)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1981)
Dow Chemical Canada, Sarnia, Ont.		60
	TOTAL	60
Domestic Production (1982)		52
Imports (1982)		0.1
	TOTAL SUPPLY	52.1

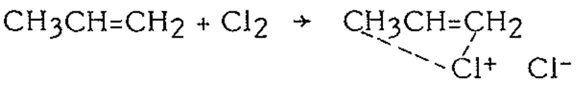
3.6 Manufacture of Propylene Oxide (Noller 1958; Corpus 1983; Kirk-Othmer 1982)

3.6.1 General (Dow 1984). Propylene oxide is currently produced at the Dow Chemical plant at Sarnia using a chlorohydrin process, with propylene and chlorine as the primary feedstocks.

3.6.2 Manufacturing Process (Kirk-Othmer 1982).

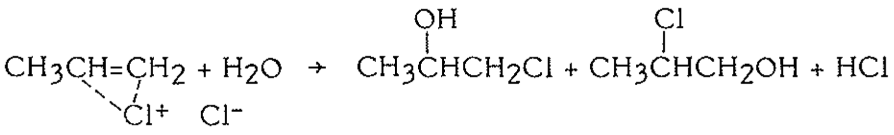
The chlorohydrin process involves the reaction of chlorine and propylene to produce a propylene-chloronium complex, reaction of water with produce chloropropanol isomers, and neutralization with a base to produce propylene oxide.

The first step is the reaction of propylene and chlorine in excess water. The most frequently proposed mechanism is one in which a propylene-chloronium complex is produced as shown below:



propylene-chloronium
complex

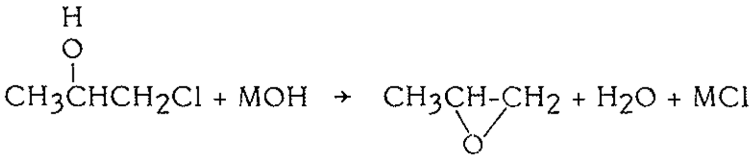
The ion complex reacts with water to form chloropropanol complexes as shown below:



90 percent
1-chloro-2-
propanol

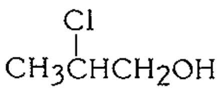
10 percent
2-chloro-1-
propanol

Both chloropropanol isomers are reacted with a base such as lime or caustic soda to produce the final product (MOH is a base):



propylene oxide

or



$CH_3\overset{Cl}{C}HCH_2OH$

3.7 Major Uses in Canada (Corpus 1983)

Propylene oxide is used in the production of polyols and propylene glycols. In 1982, 42 percent of domestic production was used for polyol production, 35 percent was exported and 19 percent was used in the production of propylene glycols.

3.8 Major Buyers in Canada (Corpus 1983)

Actol Chemicals, Delson, Que.
Alkaril Chemicals, Mississauga, Ont.
Hart Chemical, Guelph, Ont.

It should be noted that Dow Chemical uses a substantial portion of its propylene oxide at its Sarnia plant for polyol and propylene glycol production.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Transportation vessels and containers under this category have been grouped under the classification of railway tank cars and highway tank vehicles.

4.1.1.1 Railway tank cars. Railway tank cars used to transport propylene oxide are described in Table 2 (RTDCR 1974). The sole Canadian manufacturer of propylene oxide uses the 105A300W car as illustrated in Figure 7 and detailed in Table 3. The size most commonly used is the 95 000 L (21 000 imp. gal.) (Dow 1984).

The cars are unloaded from the top by pump. The liquid 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. A nitrogen pad is maintained in the tank car during shipment; when pumping out the liquid, this pad is maintained at 69-104 kPa (10-15 psi) (Dow TED 1981).

A safety relief valve set at 517 kPa (75 psi) is used on top of the rail car (Dow 1984). A closed magnetic gauging device has been installed on Canadian manufacturers' cars (Dow 1984).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
105A300W	Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Safety valve (1553 kPa) (225 psi). Bottom outlet or washout prohibited.
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi). Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi).
111A60F1	Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi). Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS (Cont'd)

CTC/DOT* Specification Number	Description
111A100W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Bottom outlet or washout optional. Test pressure 690 kPa (100 psi). Safety valve (518 kPa) (75 psi) or safety vent (690 kPa) (100 psi).
111A100W4	Steel fusion-welded tank without dome. Insulated. Gauging device. Top unloading arrangement required. Safety valve (518 kPa) (75 psi). Bottom outlet or washout prohibited.
111A60W1 (IL)	Same as 111A60W1 but interior lined.
111A100W3	Steel fusion-welded tank without dome. Insulated. 2% minimum outage. Gauging device. Safety valve (518 kPa) (75 psi) or safety vent (690 kPa) (100 psi). Bottom outlet or washout optional.

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

4.1.1.2 Tank motor vehicles. The only manufacturer in Canada does not transport propylene by truck (CCPA 1984). Propylene oxide may be transported by stainless steel or carbon steel tank motor vehicles with tanks classed as pressure vessels under Specification TC331 (Dow TED 1981). Cargo tanks under this specification are primarily for the transportation of compressed gases. These seamless or welded steel vessels must be designed and constructed in accordance with the ASME Code (TDGC 1980). Motor vehicle tanks carrying propylene oxide 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.

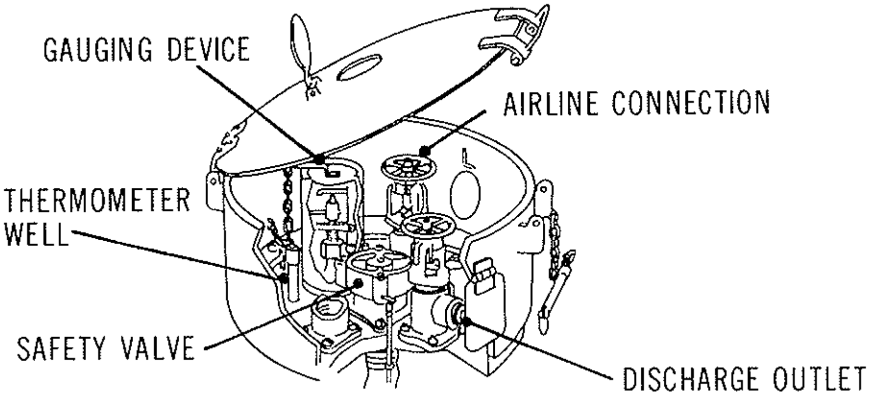
4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (Dow TED 1981):

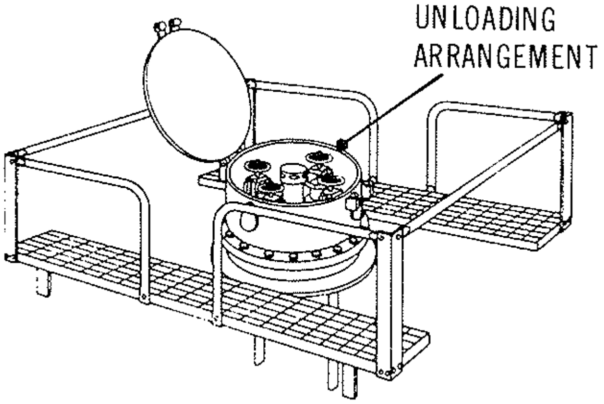
FIGURE 7

RAILWAY TANK CAR - CLASS 105A300W

(Reference - TCM 1979; RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

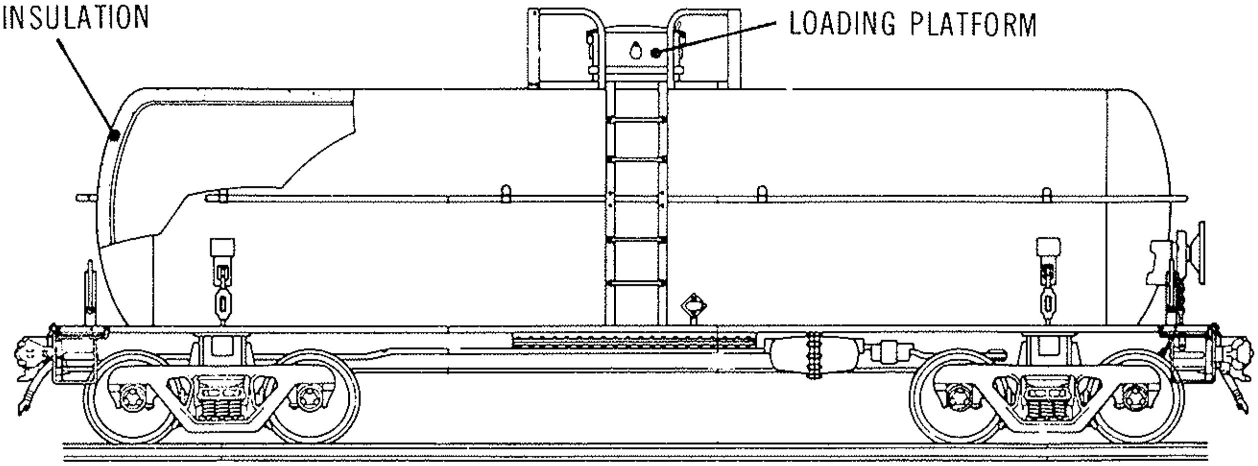


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A300W (TCM 1979; RTDCR 1974)

	Tank Car Size (Imp. Gal.)					
Description	9000		21 000		28 000	
Overall						
Nominal capacity	41 000 L	(9000 gal.)	95 000 L	(21 000 gal.)	127 000 L	(28 000 gal.)
Car weight - empty	30 300 kg	(66 800 lb.)	40 800 kg	(90 000 lb.)	50 800 kg	(112 000 lb.)
Car weight - max.	80 300 kg	(177 000 lb.)	83 500 kg	(184 000 lb.)	119 000 kg	(263 000 lb.)
Tank						
Material	Steel		Steel		Steel	
Thickness	17.5 mm	(11/16 in.)	17.5 mm	(11/16 in.)	17.5 mm	(11/16 in.)
Inside diameter	2.2 m	(88 in.)	2.4 m	(95 in.)	3.0 m	(120 in.)
Test pressure	2070 kPa	(300 psi)	2070 kPa	(300 psi)	2070 kPa	(300 psi)
Burst pressure	51 700 kPa	(750 psi)	51 700 kPa	(750 psi)	51 700 kPa	(750 psi)
Approximate Dimensions						
Coupled length	13 m	(42 ft.)	20 m	(65 ft.)	20 m	(67 ft.)
Length over strikers	12 m	(40 ft.)	19 m	(63 ft.)	20 m	(64 ft.)
Length of truck centres	9 m	(29 ft.)	16 m	(52 ft.)	16 m	(53 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)	4 m	(12 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)	5 m	(15 ft.)
Overall width	3.2 m	(127 in.)	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2 to 3 m	(7 to 10 ft.)	2 to 3 m	(7 to 10 ft.)	2 to 3 m	(7 to 10 ft.)
Width of grating	1.5 to 2 m	(5 to 6 ft.)	1.5 to 2 m	(5 to 6 ft.)	1.5 to 2 m	(5 to 6 ft.)
Loading/Unloading Fixtures						
Unloading connection	51 mm (2 in.) via valve and 76 mm (3 in.) check valve; 6 mm (1/4 in.) outlet					
Valving	2 unloading connections and 2 valves to vapour space					
Gauging Device	Float-type or sealed magnetic type					
Safety Devices	Safety relief valve set at 517 kPa (75 psi) (special for propylene service, normally 1550 kPa)					
Insulation	51 to 152 mm (2 to 6 in.) fibreglass insulation					

- The storage tank must be checked to make sure that it will hold the contents of the car.
- Lights, pumps and all other equipment 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.
- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- Effectively ground the tank car.

Off-loading is only recommended for top connections (CCPA 1984). Proceed with top off-loading as follows (Dow TED 1981):

- Maintain nitrogen gas blanket at 69 to 104 kPa (10-15 psi).
- After removing the protective housing from the discharge line at top of car, connect the 50 mm unloading line.
- Off-load the tanker by pump only.

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. It is recognized that other materials may be used for particular applications as indicated in Table 4. 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 and fittings lined with polyvinylidene chloride (Saran) resins are recommended (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. Bonding is required across the flange to ensure electrical conductivity. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipeline should be tested with air at pressures up to 172 kPa (25 psi) and all leaks carefully stopped. The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on these tank cars; but process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining. Stainless steel or carbon steel flex hoses should be used for the flexible sections of the unloading line (CCPA 1984).

Cast iron or cast steel diaphragm valves lined with polyvinylidene chloride resin will serve adequately (DPLV 1972). Spiral-wound Teflon should be used as a gasket material at normal temperature ranges (Dow TED 1981).

A single-suction rotary or centrifugal pump with "wet end" material of 316 stainless steel gives good results (Dow TED 1981). Provision must be made for draining the pump so that repairs can be made safely. The pump should be equipped with flanges at both suction and discharge openings; screw connections are more subject to leakage and should be avoided.

4.3 Compatibility with Materials of Construction

The compatibility of propylene oxide with materials of construction is indicated in Table 4. The unbracketed abbreviations are described in Table 5. The rating system for this report is briefly described below:

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

TABLE 4 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	All	24	PVDC (DCRG 1978)		
					PVDF (DCRG 1978)
			SS CS (Dow TED 1981)		
2. Valves	All	Most	SS (Dow TED 1981)		
3. Pumps	All	Most	SS CS Ductile Iron (Dow TED 1981)		
4. Storage	All	Most	SS CS CS lined (Dow TED 1981)		Copper (Dow TED 1981)

TABLE 4 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others	100%	24 to 100	Glass (CDS 1967) PTFE (Dow TED 1981)		Aluminum (CCPA 1984)

TABLE 5 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
	Aluminum
CS	Carbon Steel
	Ductile Iron
	Fluorine Rubber (Viton)
	Glass
	Nickel-Copper Alloy (Monel)
PTFE	Polytetrafluoroethylene
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SS (followed by grade)	Stainless Steel

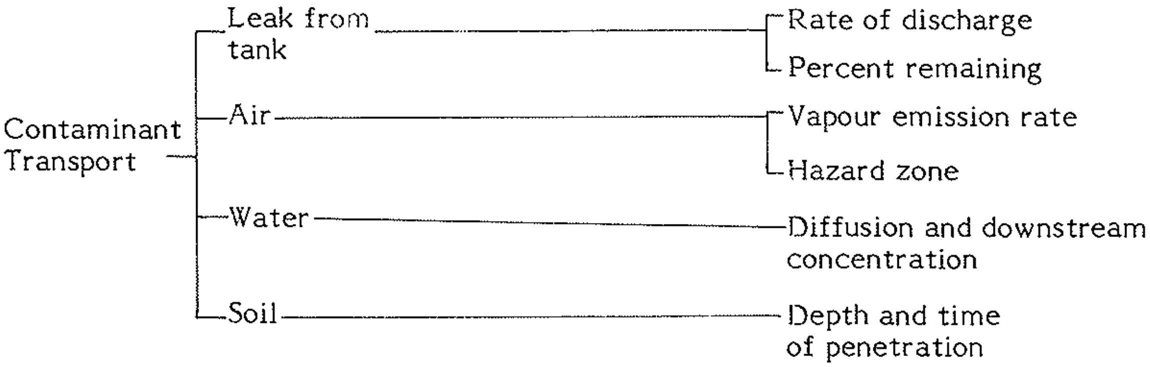
5 CONTAMINANT TRANSPORT

5.1 General Summary

Propylene oxide is a liquid which is soluble in and less dense than water. When spilled on water, propylene oxide will dissolve quickly, with some evaporation to the atmosphere. When spilled on water or soil, the vapour cloud tends to hug the surface and spread, rather than lift off the ground and disperse. The vapour is both flammable and a health hazard.

Propylene oxide spills on soil surfaces will partly vapourize and partly adsorb onto the soil at a rate dependent on the soil type and its degree of saturation with water. Downward transport toward the groundwater table may cause environmental concerns.

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



5.2 Leak Nomograms

5.2.1 Introduction. Propylene oxide is commonly transported as a liquid at ambient temperature. While the capacities of the railway tank cars vary widely, one 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 propylene oxide is punctured on the bottom, all of the contents will drain out. The instantaneous discharge rate (q) is a function of the height of the fluid above the hole (H), the internal pressure of the tank (P), the hole area (A) and shape, and a coefficient of discharge (C_d). For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

At the assumed maximum tank contents temperature of 40°C, the saturated vapour pressure (P_{sat}) of propylene oxide is 124 kPa. Under these conditions, if the tank car is punctured in the top or at any point above the liquid level, gas will be vented until all of the liquid has vaporized and the internal and external tank pressures have equalized. For the purposes of nomogram preparation, the liquid is assumed to remain at a constant temperature (isothermal) equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid is vaporized. The venting rate is a function of the internal tank pressure (P), which is equal to the saturated vapour pressure (P_{sat}) of the liquid at temperature T.

The assumption of isothermal conditions will maximize the gas release rate from the tank and will be conservative for most cases. Under some spill circumstances, evaporative cooling will slow the rate to as much as an order of magnitude from that predicted here.

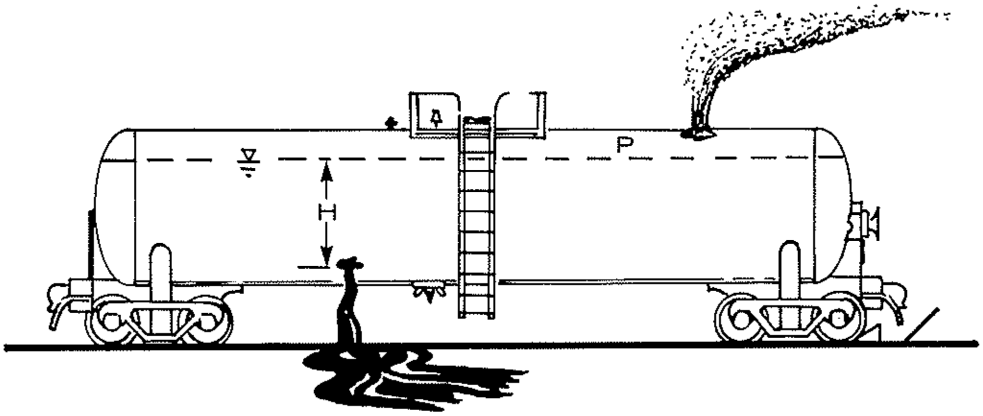


FIGURE 8 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

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

5.2.2 Nomograms.

5.2.2.1 Bottom puncture - liquid venting.

Figure 9: Percent remaining versus time. Figure 9 provides a means of estimating the percent of propylene oxide 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 propylene oxide at 40°C. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

Figure 10: Discharge rate versus puncture size. Figure 10 provides a means of estimating the maximum discharge rate (L/s) for a number of equivalent hole diameters. As the pressure force dominates the gravitational force, the discharge rate remains relatively constant as the tank empties.

5.2.2.2 Top puncture - gas venting.

Figure 11: Percent remaining versus time. Figure 11 provides a means of estimating the percent of propylene oxide remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture. As isothermal conditions have been assumed, the internal pressure and venting rate are constant.

Figure 12: Discharge rate versus puncture size. Figure 12 presents the relationship between discharge rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For any one hole size, the venting rate will be constant until all the liquid has vaporized. This is consistent with the assumption of isothermal conditions in the tank and results in a conservative estimate of the gas venting rate. The values presented in Figure 12 are independent of the tank car size, but assume that the temperature of the liquid is 40°C, yielding a saturated vapour pressure of 124 kPa.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with propylene oxide at 40°C has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 3 minutes and what is the instantaneous discharge rate from the tank?

Solution to Problem A

Step 1: Calculate amount remaining at t=3 min

- Use Figure 9

FIGURE 9

PROPYLENE OXIDE

PERCENT REMAINING vs TIME

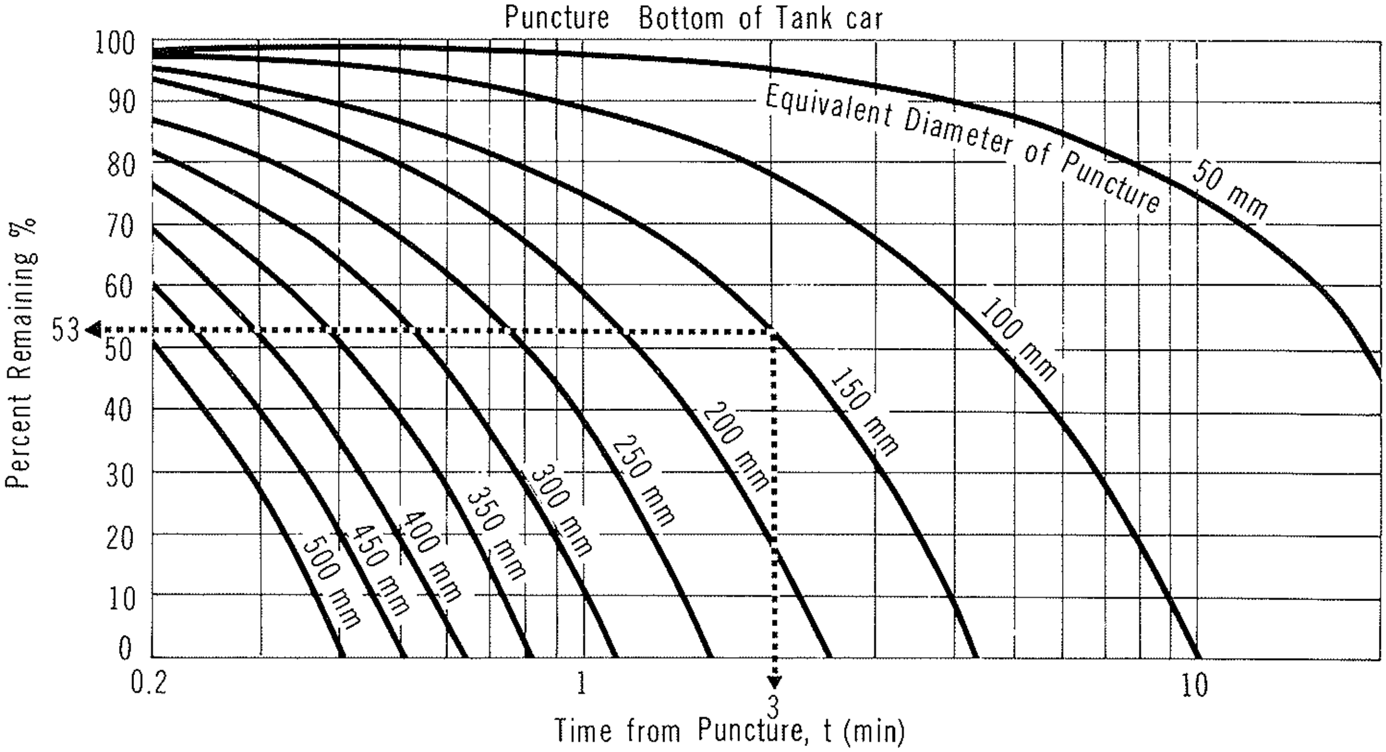


FIGURE 10

PROPYLENE OXIDE

DISCHARGE RATE vs PUNCTURE SIZE

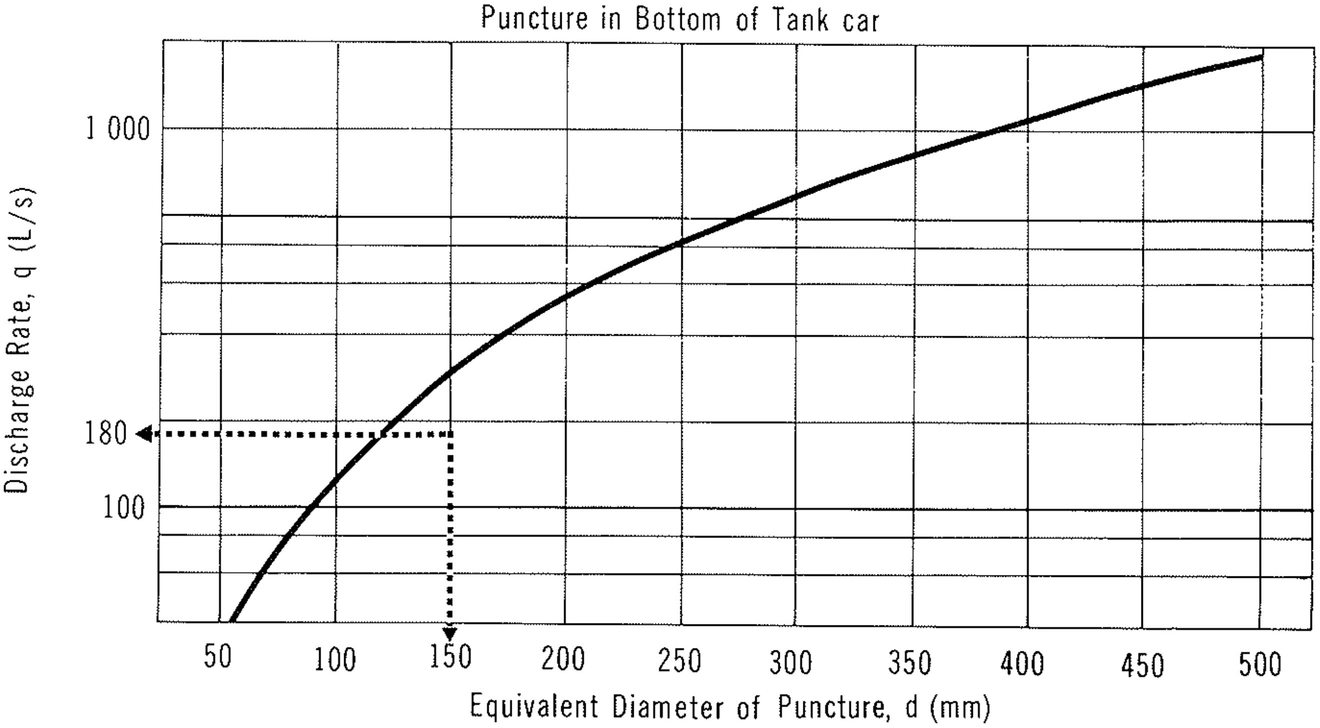


FIGURE 11

PROPYLENE OXIDE

PERCENT REMAINING vs TIME

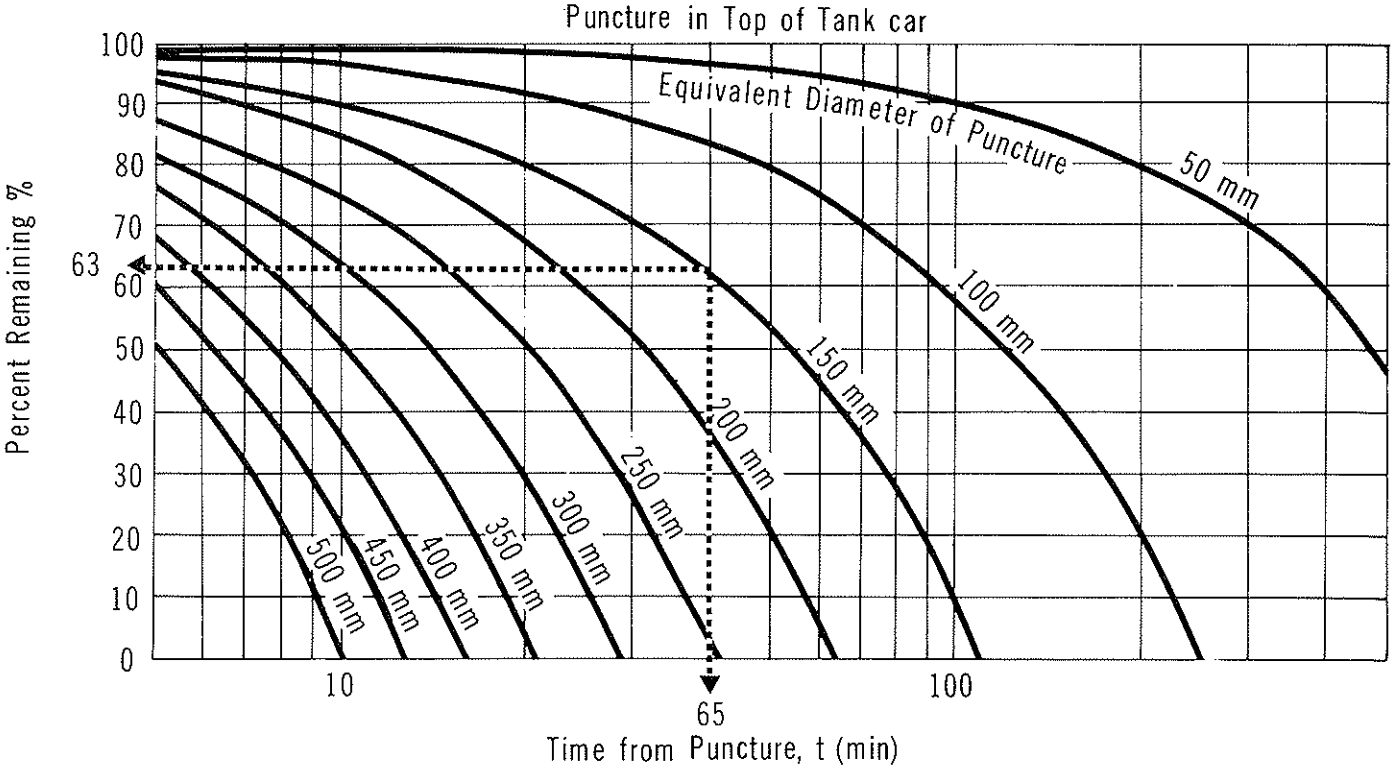
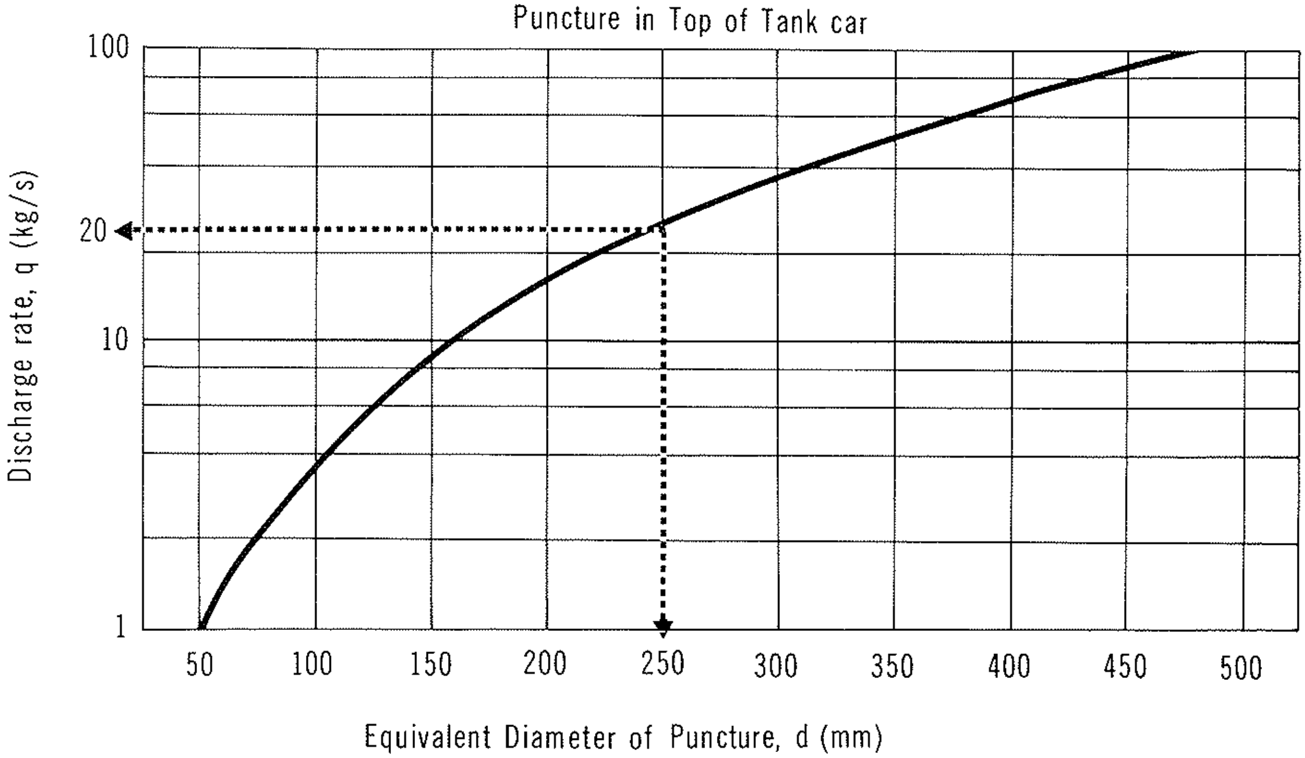


FIGURE 12

PROPYLENE OXIDE

DISCHARGE RATE vs PUNCTURE SIZE



- With t=3 min and d=150 mm, the amount remaining is about 53 percent or 42 400 L

Step 2: Calculate the discharge rate

- Use Figure 10
- With d=150 mm, the instantaneous discharge rate (q) = 180 L/s

ii) Problem B

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

Solution to Problem B

Step 1: Calculate the time to empty

- Use Figure 11
- With d=250 mm, the tank empties (0 percent remaining) in approximately 65 min

Step 2: Calculate the discharge rate

- Use Figure 12
- With d=250 mm and assuming isothermal conditions, the venting rate is constant at 20 kg/s

5.3 Dispersion in the Air

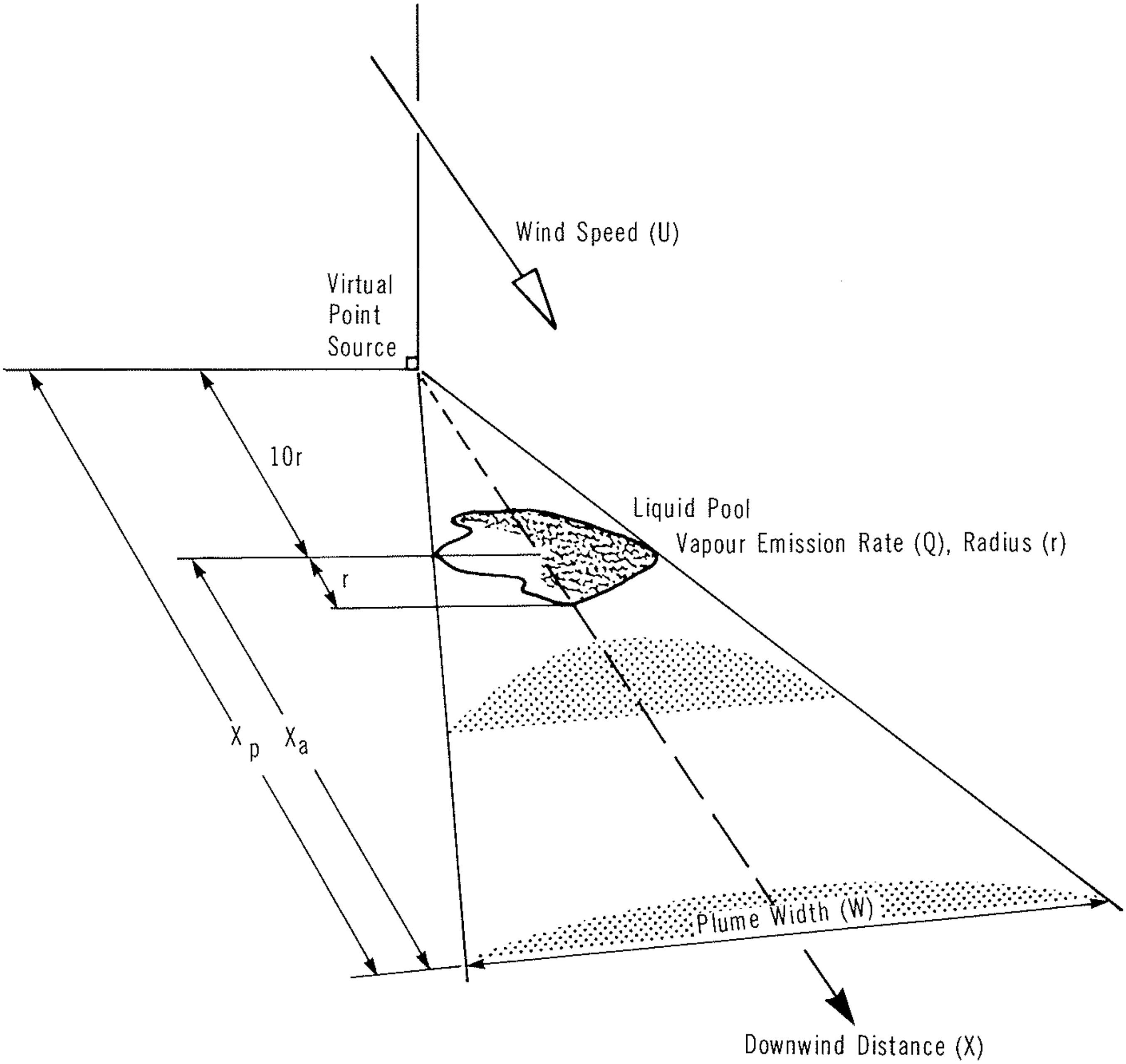
5.3.1 Introduction. Although propylene oxide is a relatively volatile liquid, direct venting of the vapour to the atmosphere from a hole in a punctured vessel does not constitute a significant hazard downwind. Only vapour released from a liquid pool spilled on a ground or water surface is treated here.

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 13 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.

FIGURE 13

SCHEMATIC OF CONTAMINANT PLUME



It should be noted that although propylene oxide has a low boiling point for a liquid (34°C at 1 atm), the plume dispersion scenario rather than the puff dispersion scenario has been used to estimate the hazard zone. Under most spill situations, the vapour release rate from an instantaneously formed liquid pool would be continuous in nature and therefore the plume dispersion modelling would apply. The conditions under which an instantaneous puff would be released (e.g., ambient and ground temperature 34°C, no evaporative cooling, and a rapidly moving liquid spill) are considered remote and would not occur in forseeable spill situations.

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

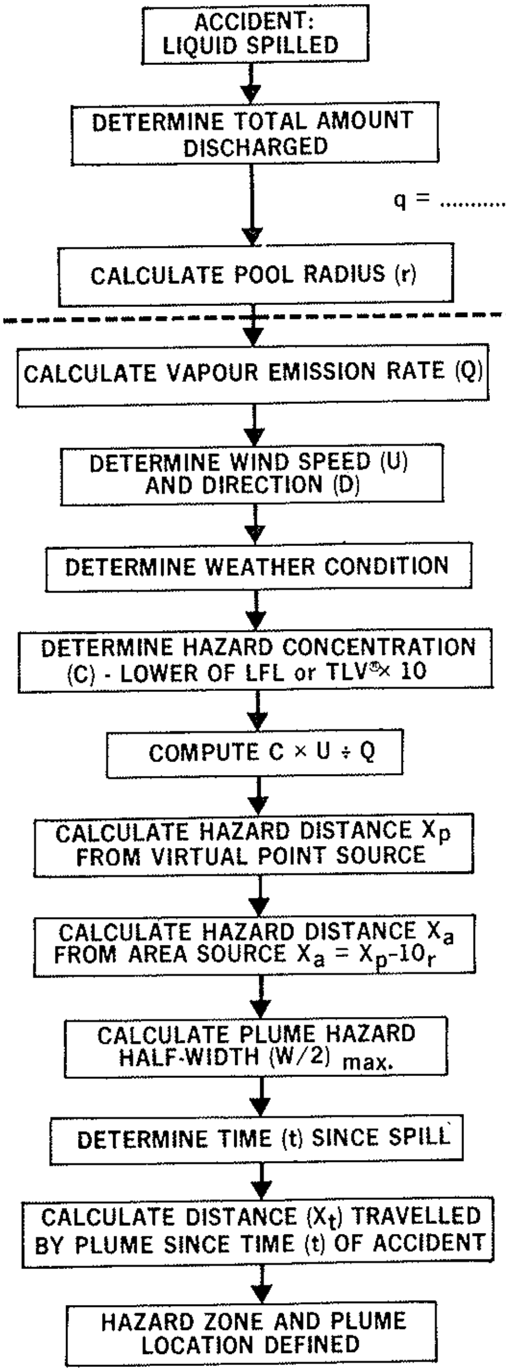
Figure 15:	vapour emission rate from a liquid pool as a function of maximum pool radius
Table 6:	weather conditions
Figure 16:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 7:	maximum plume hazard half-widths
Figure 19:	vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 14 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 15: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for propylene oxide has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for propylene oxide at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 11.5 g/(m^2s). 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 (Chem. Eng. 1976) of propylene oxide at that temperature. For example, evaporation rates of 5.0 g/(m^2s) at 0°C and 15.0 g/(m^2s) at 30°C were calculated for a wind speed of 4.5 m/s.

FIGURE 14

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE



Step 1: Use Figure 9 Section 5.2

Time since rupture .... minutes
Equivalent diameter of rupture .... mm
Percent of chemical remaining .... %
Amount discharged:
q = 80 000 L - % × 80 000 L = ... L
q = ... L × density (kg/L) ÷ 1000 = ... tonnes

Step 2: Use 2 mm pool thickness
r = ... km

Step 3: Use Figure 15
Q = ... g/s

Step 4: Observed or estimated
U = ... km/h; D = ... degrees

Step 5: Use Table 6 Condition = ...

Step 6:

Step 7: Computation required
CU/Q = ... m^{-2}

Step 8: Use Fiqure 16
X_p = ... km

Step 9: Computation required
X_a = ... m

Step 10: Use Table 7
$(W/2)_{max.}$ = ... m

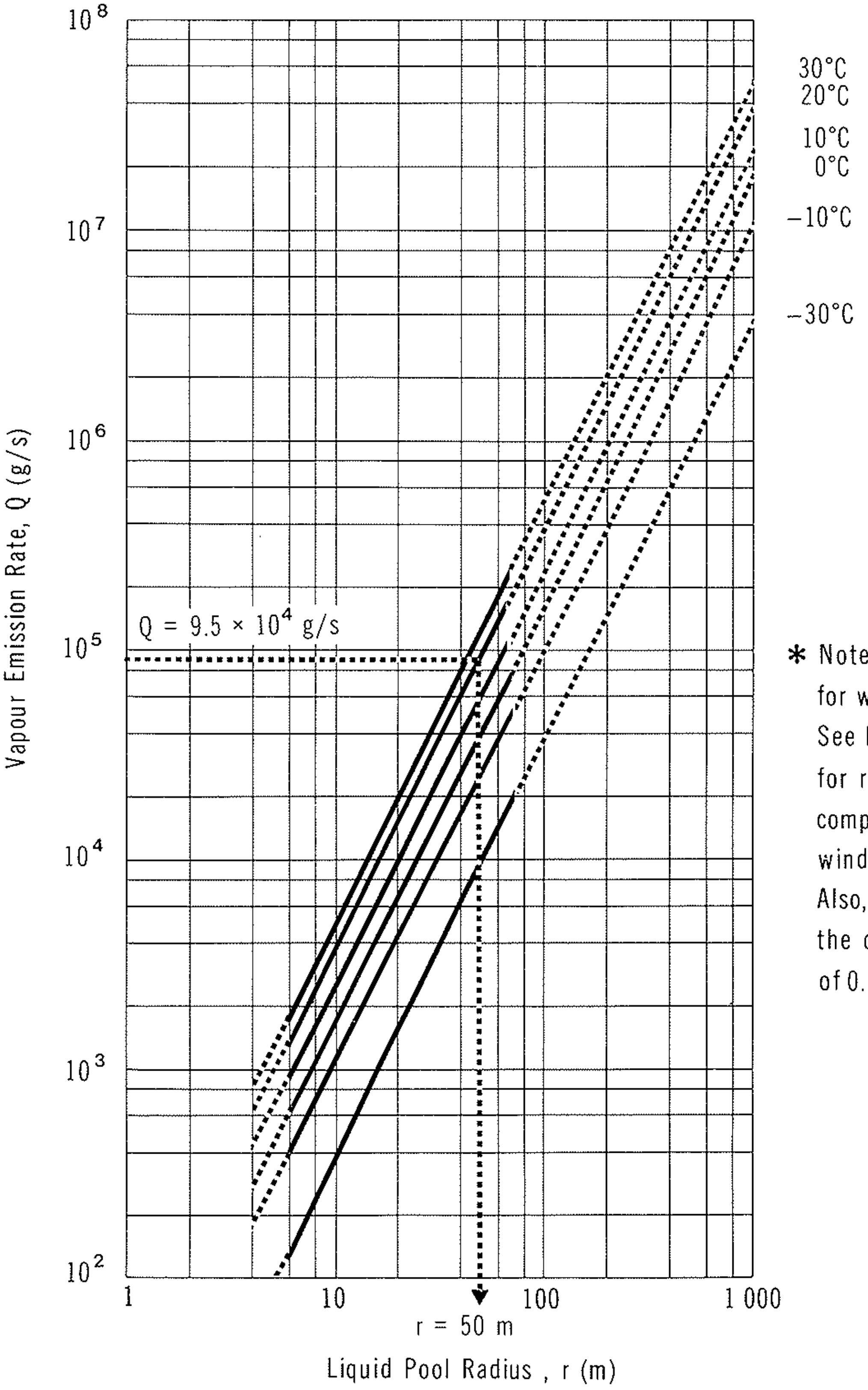
Step 11: t = ... s

Step 12: Use Figure 19 with U from Step 4.
X_t = ... km

FIGURE 15

PROPYLENE OXIDE

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 0.05 to 66 tonnes.

Use: For a pool of propylene oxide of known radius, the rate (Q) at which propylene oxide vapour is released to the atmosphere at a given temperature can then be estimated from Figure 15. The solid portions of the curves represent spills of 0.05 to 66 tonnes, the latter representing about one standard 80 000 L (17 600 Imp. gal.) rail car load of propylene oxide. It should be noted that Figure 15 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 propylene 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.

It should also be noted that the determination of the emission rate is based on the spill radius on calm water (Table D1, CHRIS 1974). The spill radius employed was that of ethyl nitrite, since the vapour pressure and specific gravity of propylene oxide are similar to that of ethyl nitrite. 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 16: Normalized vapour concentration versus downwind distance.

Figure 16 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 16, the weather condition must be determined from Table 6.

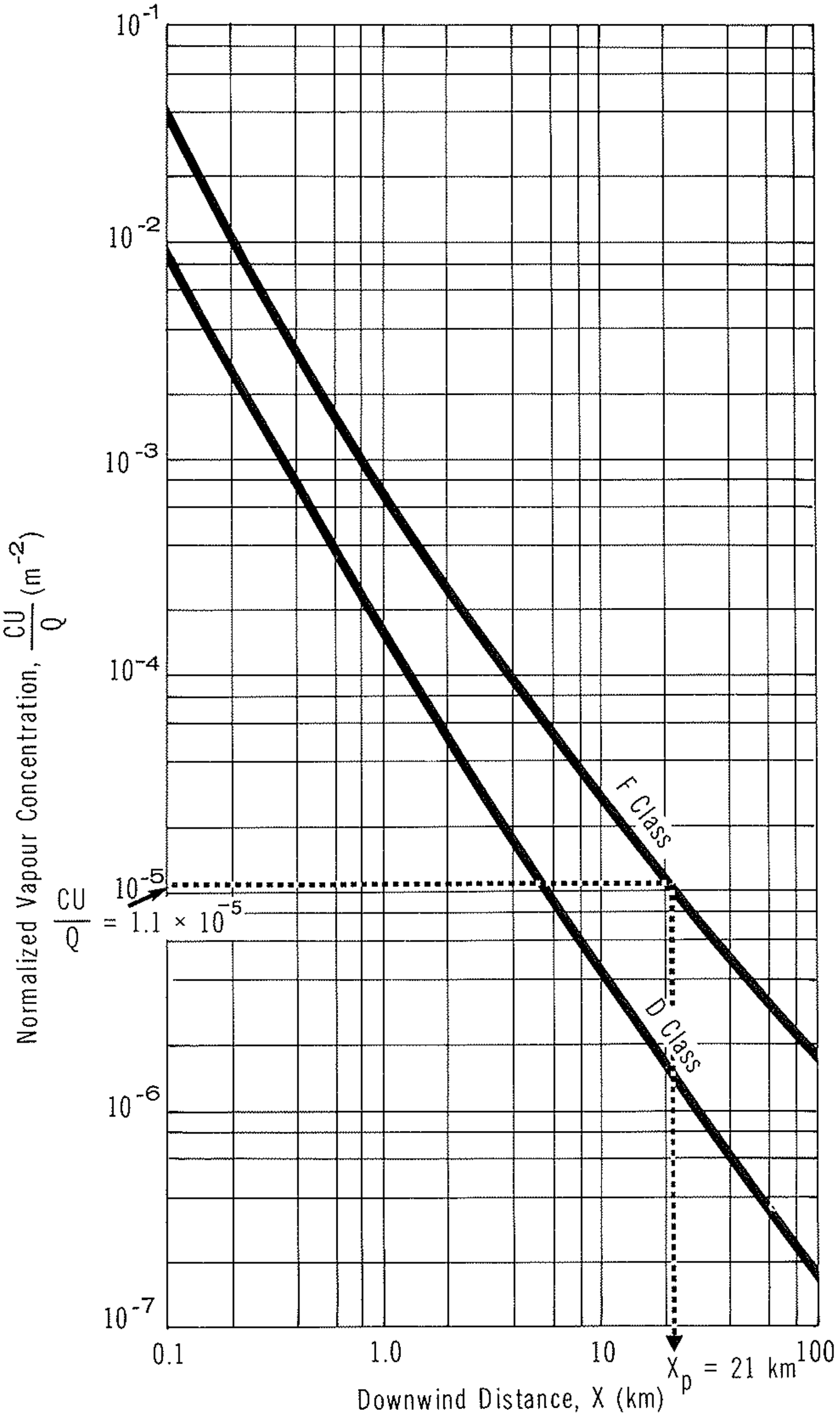
TABLE 6 WEATHER CONDITIONS

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

FIGURE 16

PROPYLENE OXIDE

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



Use: The maximum hazard distance, X_p, downwind of the spill can be calculated from Figure 16 knowing:

- Q, the vapour emission rate (g/s)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value (TLV®, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3). Note: To convert the TLV®, in ppm, and the LFL, in percent by volume, to concentrations in g/m^3, use Figures 17 and 18

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.

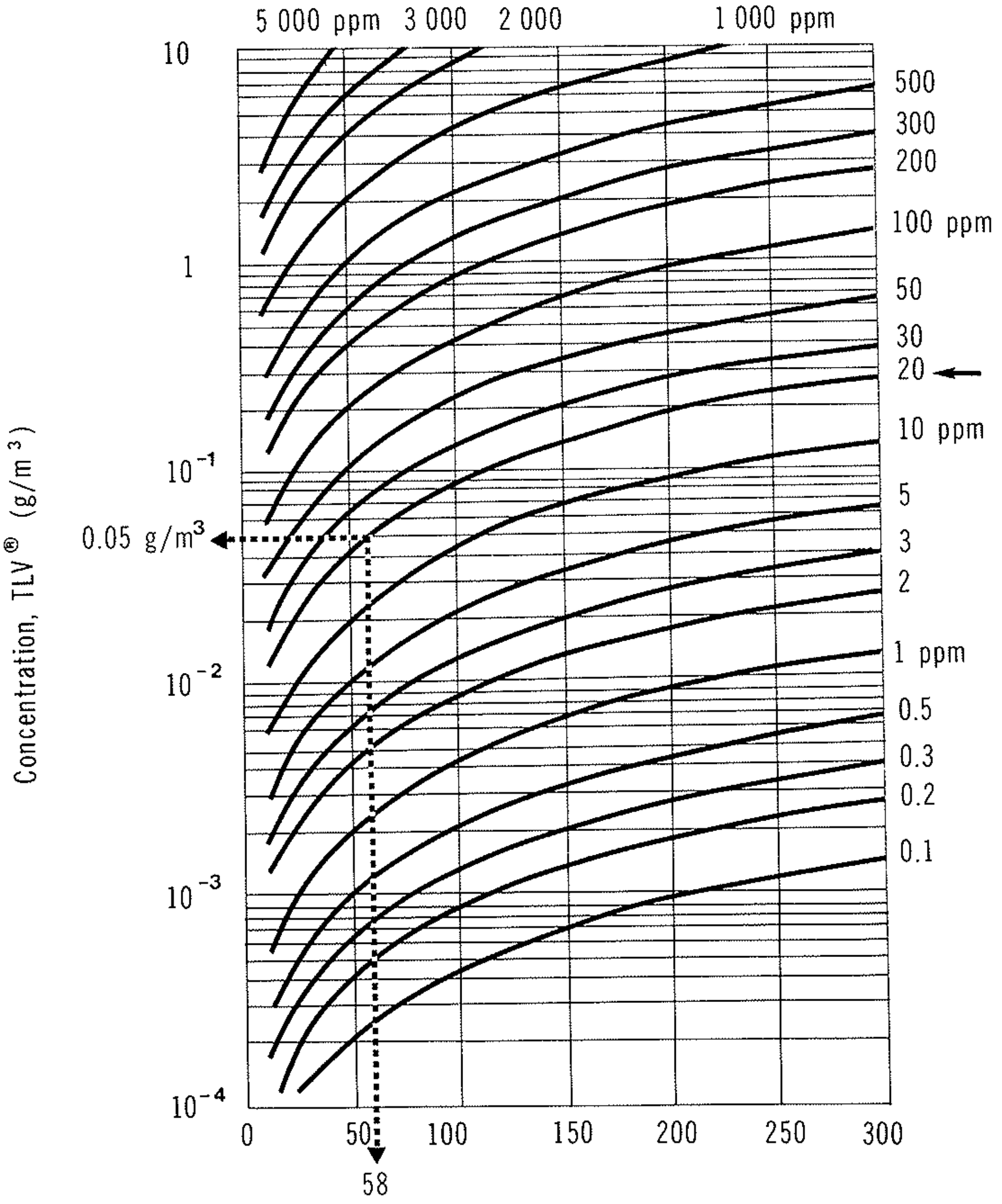
5.3.2.3 Table 7: Maximum plume hazard half-widths. This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the propylene oxide Threshold Limit Value (TLV®) of 0.05 g/m^3, or 0.50 g/m^3. The maximum plume hazard half-width represents the maximum half-width of the propylene oxide vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 7 is therefore only applicable for a propylene oxide hazard concentration limit of 10 x TLV® or 0.50 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 7500 to 3 500 000 g/s, corresponding to propylene oxide spills in the range of about 1 to 2500 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spills, the mass spilled would be 66 400 kg or approximately 66 tonnes. Therefore, under class D of Table 7, data are provided for up to about 37 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 750 to 300 000 g/s, corresponding to propylene oxide spills in the range of about 0.05 to 100 tonnes, respectively. Therefore, under class F of Table 7, data are provided for up to 1.5 times a standard rail car load.

FIGURE 17

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



Molecular Weight

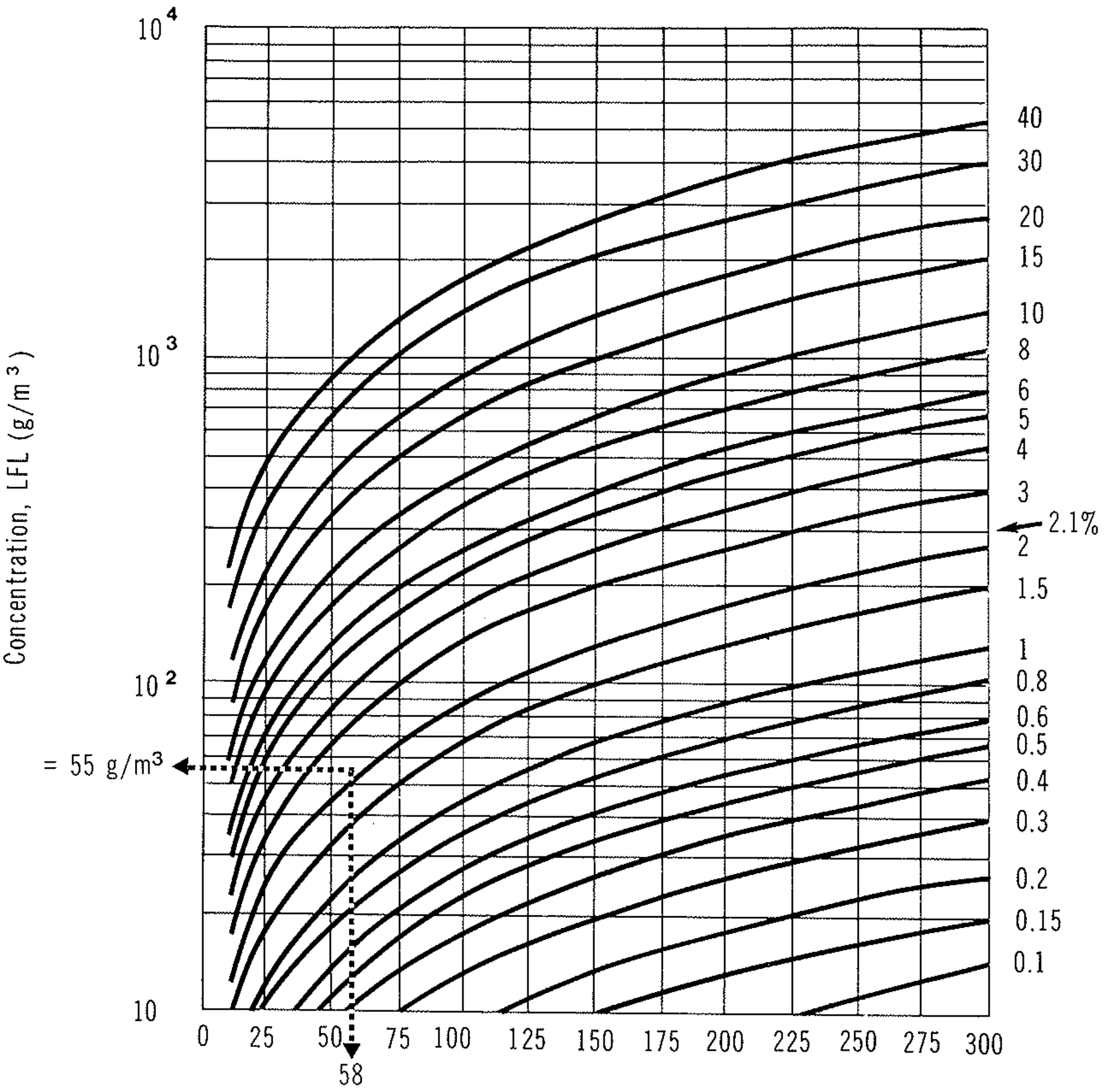
Example: Propylene oxide, MW = 58, TLV® = 20 ppm, then TLV® in g/m³ =0.05

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

FIGURE 18

PROPYLENE OXIDE

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



Example: Propylene Oxide, MW = 58, LFL = 2.1%, then LFL in g/m³= 55

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

TABLE 7 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR PROPYLENE OXIDE 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)	
3 500 000	3430	(99.5 km)*	300 000	1430	(99.5 km)*
3 000 000	3115		250 000	1250	
2 500 000	2785		200 000	1060	
2 000 000	2425		150 000	855	
1 500 000	2030		125 000	745	
1 250 000	1815		100 000	630	
1 000 000	1580		75 000	510	
750 000	1320	Q/U = 45 200 →	50 000	375	→ $(W/2)_{max} = 375$ m
500 000	1030		25 000	240	
300 000	750		10 000	135	
200 000	585		7 500	110	
150 000	500		5 000	85	
100 000	395		2 500	55	
75 000	335		1 000	35	
50 000	260		500	25	
25 000	175		250	15	
10 000	100				
5 000	70				
2 500	50				
1 000	30				
500	20				
250	15				

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

Example: A spill releasing propylene oxide vapour at the rate of $Q = 9.5 \times 10^4$ g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 45 200 g/m which results in a maximum plume hazard half-width $(W/2)_{max} = 375$ m.

Note: Above table is valid only for a propylene oxide concentration of 10 x TLV®, or 0.5 g/m^3.

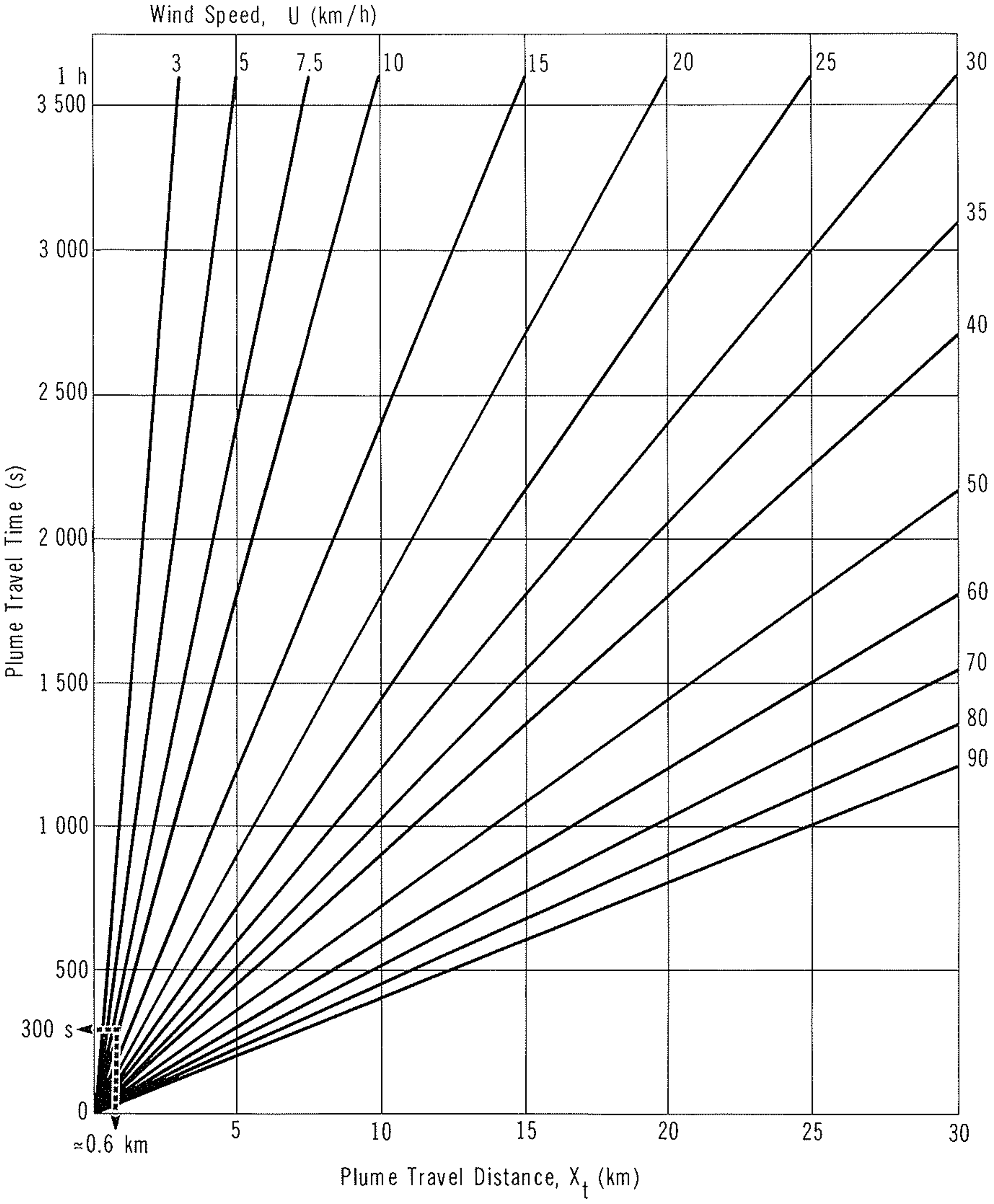
Use: Knowing the weather condition, Q and U, compute Q/U. Choose the closest Q/U value in the table and the corresponding $(W/2)_{max}$, the maximum plume hazard half-width, in metres. (For an intermediate value, interpolate Q/U and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 7.

5.3.2.4 Figure 19: Plume travel time versus travel distance. Figure 19 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.

FIGURE 19

PROPYLENE OXIDE

PLUME TRAVEL TIME VS TRAVEL DISTANCE



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 propylene oxide. 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 propylene oxide 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 the observed (measured) pool radius if possible. If not, use the maximum radius calculated assuming a 2 mm spill thickness
- Radius (r) = 50 m ÷ 1000 = 0.05 km

Step 3: Calculate the vapour emission rate (Q) at T = 20°C

- From Figure 15, for r = 50 m and T = 20°C, Q = 9.5×10^4 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 ÷ 3.6 = 2.1 m/s

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

Step 5: Determine the weather condition

- From Table 6, weather condition = F since U is less than 11 km/h and it is night

Step 6: Determine the hazard concentration limit (C)

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

  C = 0.50 g/m^3 (TLV® = 0.05 g/m^3; LFL = 55 g/m^3)

Step 7: Compute CU/Q

- $CU/Q = \frac{0.01 \times 2.1}{1.3 \times 10^4} = 1.1 \times 10^{-5}\ m^{-2}$

Step 8: Calculate the downwind distance (X_p) from the virtual point source

- From Figure 16, with $CU/Q = 1.1 \times 10^{-5}\ m^{-2}$ and weather condition F, $X_p \simeq 21$ km

Step 9: Calculate the hazard distance (X_p) downwind of the area source

- With $X_p = 21$ km and r = 0.05 km, then
  $X_a = X_p - 10\ r = 21\ km - 10\ (0.05\ km) = 20.5\ km$

Step 10: Calculate the plume hazard half-width $(W/2)_{max}$

- Use Table 7
- With $Q = 9.5 \times 10^4$ g/s and U = 2.1 m/s
  then $Q/U = \frac{9.5 \times 10^4}{2.1} = 45\ 200$ g/m
- Then for weather condition F, the closest Q/U value is 50 000 g/m, which gives $(W/2)_{max} \simeq 375$ m

Step 11: Determine the time since the spill

- t = 5 min x 60 = 300 s

Step 12: Calculate the distance travelled (X_t) by the vapour plume since the time of the accident

- Using Figure 19, with t = 300 s and U = 7.5 km/h,
  then $X_t = 0.6$ km (more accurately from Ut = 2.1 m/s x 300 s = 630 m = 0.63 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 (375 m) by the maximum hazard distance downwind of the area source (20.5 km) along the direction of the wind, as shown in Figure 20
- 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 21
- 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 160 minutes before the plume reaches the maximum downwind hazard distance of 20.5 km

FIGURE 20

PROPYLENE OXIDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

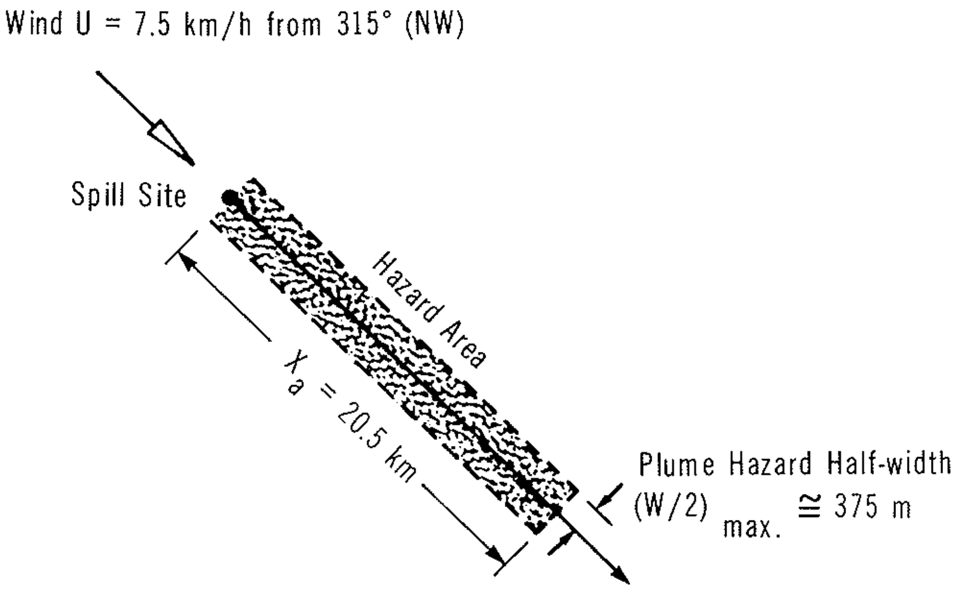
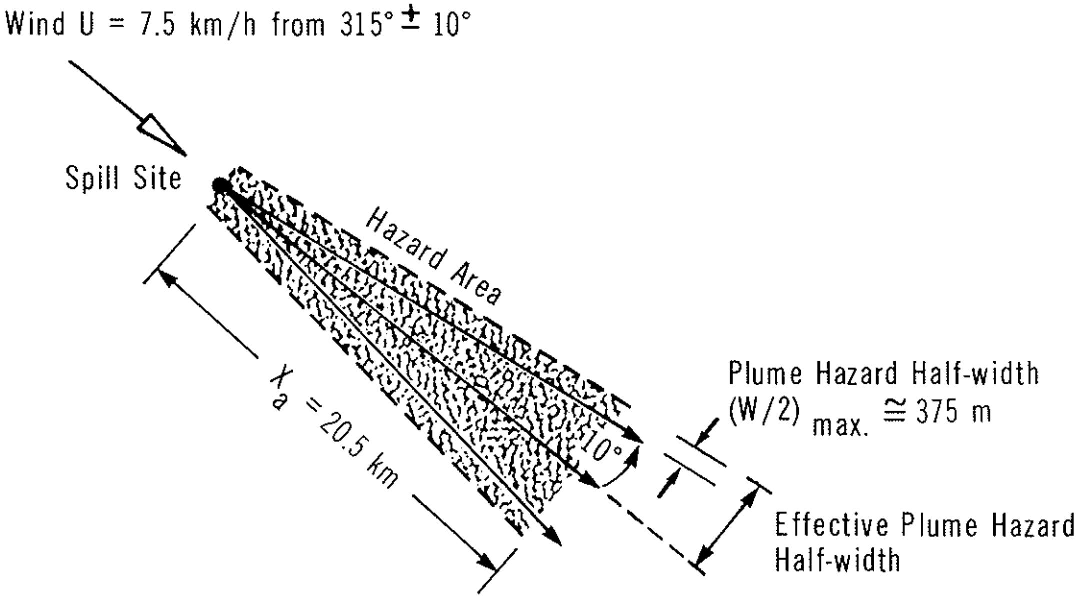


FIGURE 21

PROPYLENE OXIDE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM



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

$= 20.5 \times 1000 \times \tan 10° + 375$ m

$= 3990$ m or 4.0 km

5.4 Behaviour in Water

5.4.1 Introduction. A spill of propylene oxide on water will initially float on the surface. Because the chemical is soluble in water, part will dissolve readily and part will evaporate. Mixing takes place and the spill is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence while in calm water mixing takes place by molecular diffusion.

To estimate 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.

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 pollutant concentrations in non-tidal rivers and in lakes (still water).

Non-Tidal Rivers

Figure 23:	time versus distance for a range of average stream velocities
Figure 24:	hydraulic radius versus channel width for a range of stream depths
Figure 25:	diffusion coefficient versus hyraulic radius for a range of average stream velocities
Figure 26:	alpha* versus diffusion coefficient for various time intervals
Figure 27:	alpha versus delta* for a range of spill sizes
Figure 28:	maximum concentration versus delta for a range of river cross-sectional areas

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

Lakes or Still Water Bodies

Figure 29:	volume versus radius for the hazard zone for a range of lake depths
Figure 30:	average concentration versus volume for the hazard zone for a range of spill sizes

The flowchart in Figure 22 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figure 23 through 30) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 23: Time versus distance. Figure 23 presents a simple relationship between average 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 23.

Figure 24: 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 24 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 25: Diffusion coefficient versus hydraulic radius. Figure 25 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 24 and the average stream velocity (U).

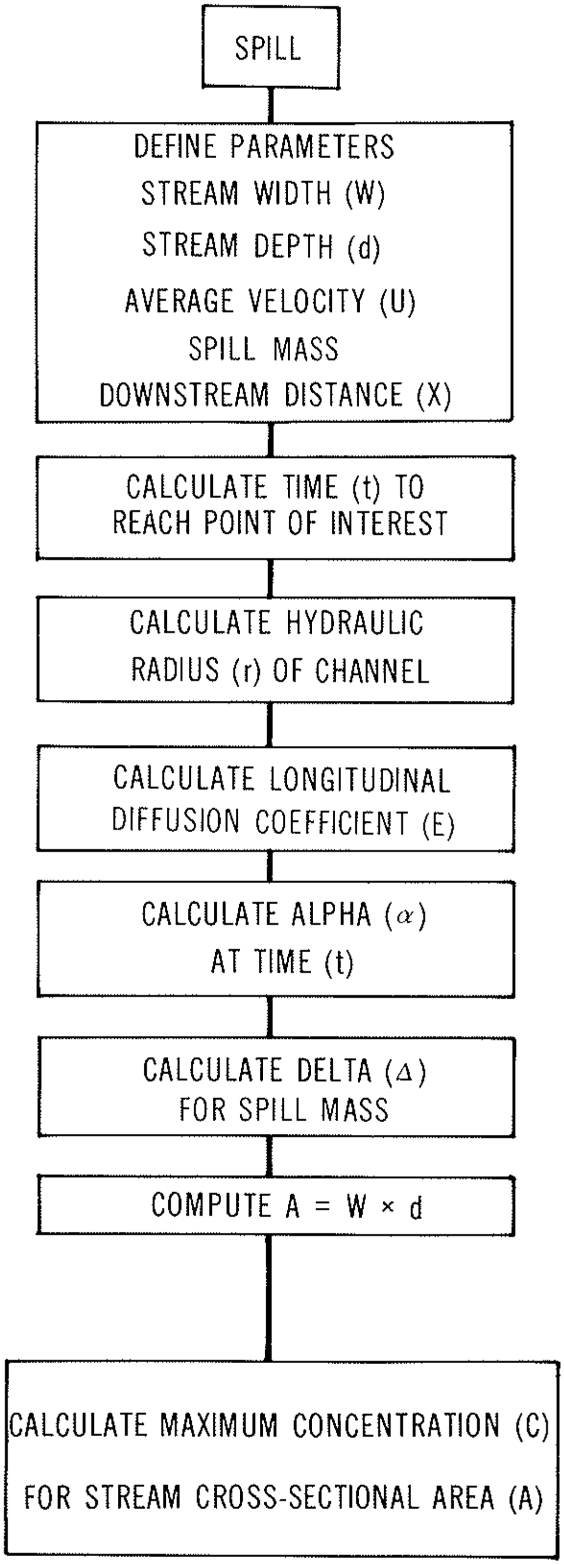
Figure 26: Alpha versus diffusion coefficient. Figure 26 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 27: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 27 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 28: Maximum concentration versus delta. Figure 28 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

FIGURE 22

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS



Step 1: Observed or Estimated

$W =$ ________ m

$d =$ ________ m

$U =$ ________ m/s

MASS = ________ tonnes

$X =$ ________ m

Step 2: Use Figure 23

$t =$ ________ minutes

Step 3: Use Figure 24

$r =$ ________ m

Step 4: Use Figure 25

$E =$ ________ m^2/s

Step 5: Use Figure 26

$\alpha =$ ________

Step 6: Use Figure 27

$\Delta =$ ________

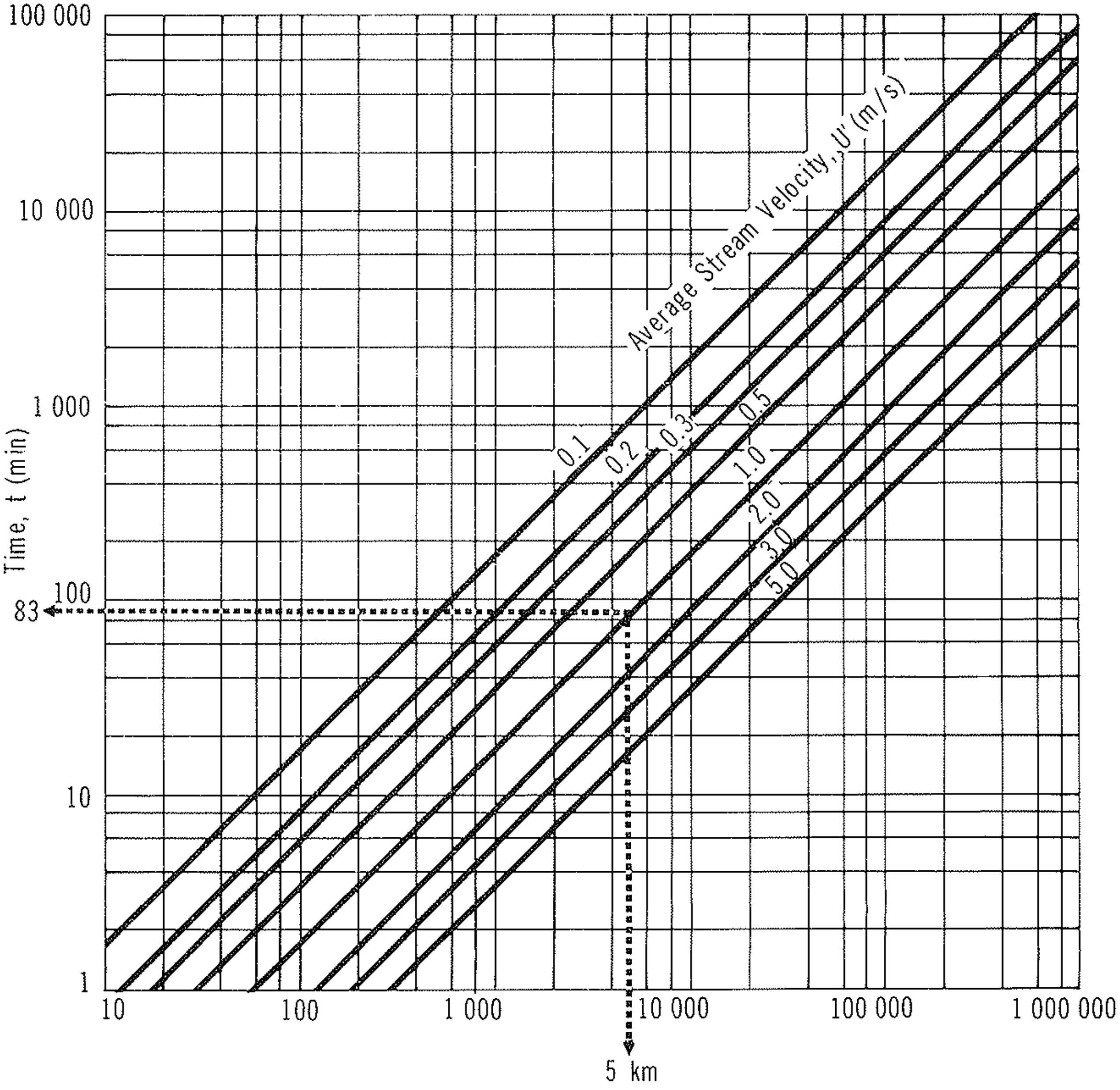
Step 7: Compute stream cross-sectional Area (A)

$A = W \times d$ ______ m^2

Step 8: Use Figure 28

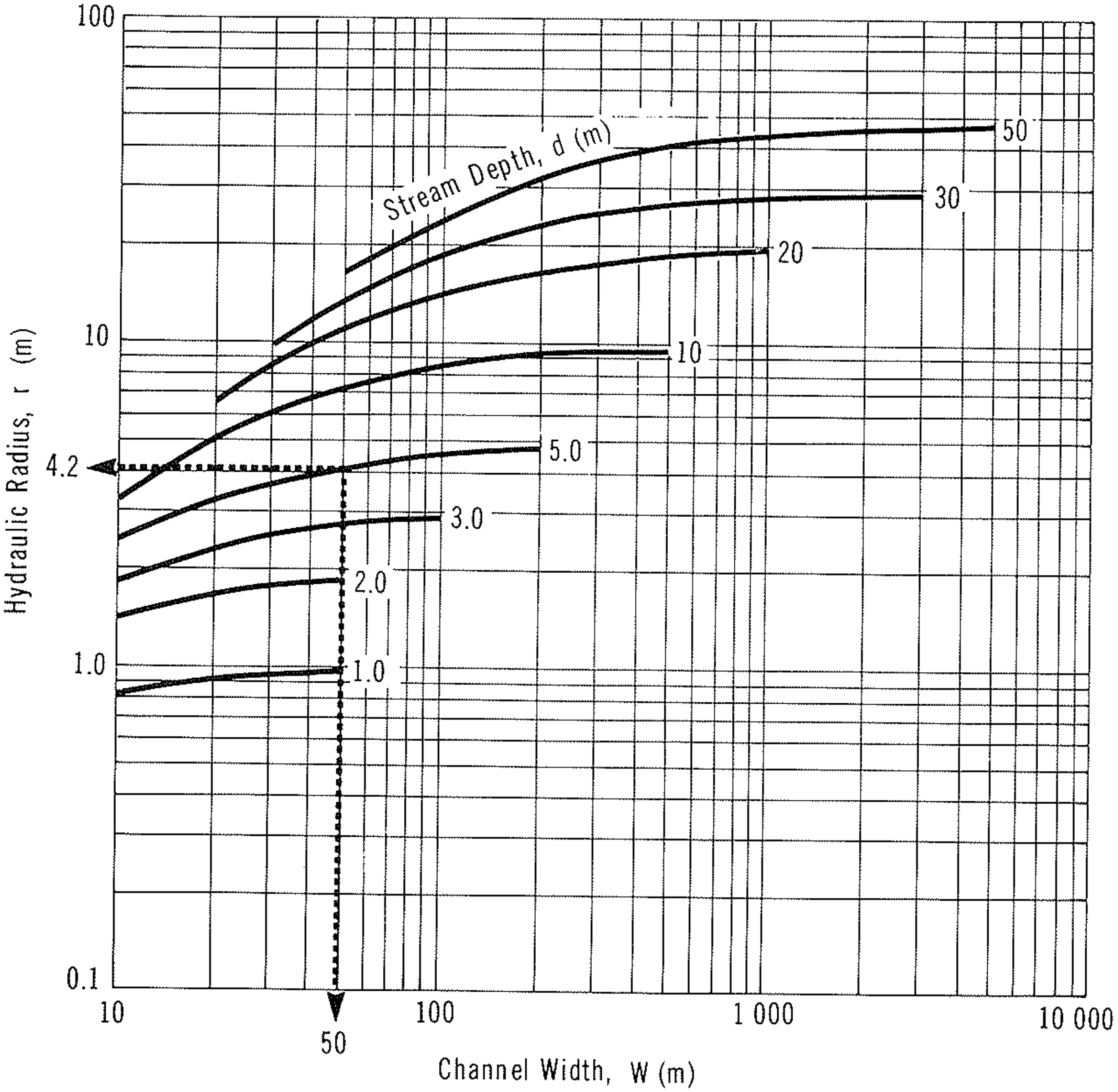
$C =$ ________ ppm

TIME vs DISTANCE

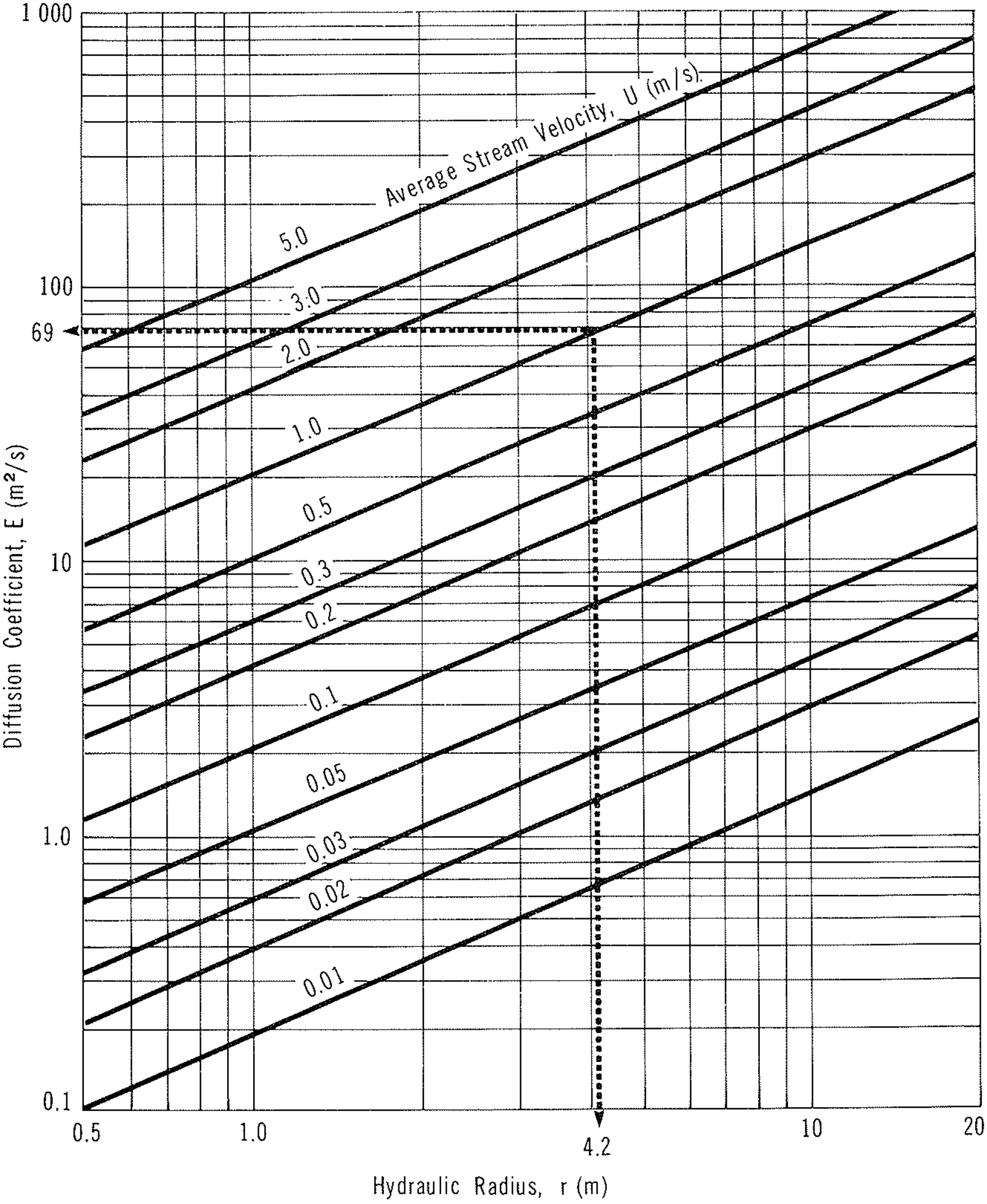


Distance, X (m)

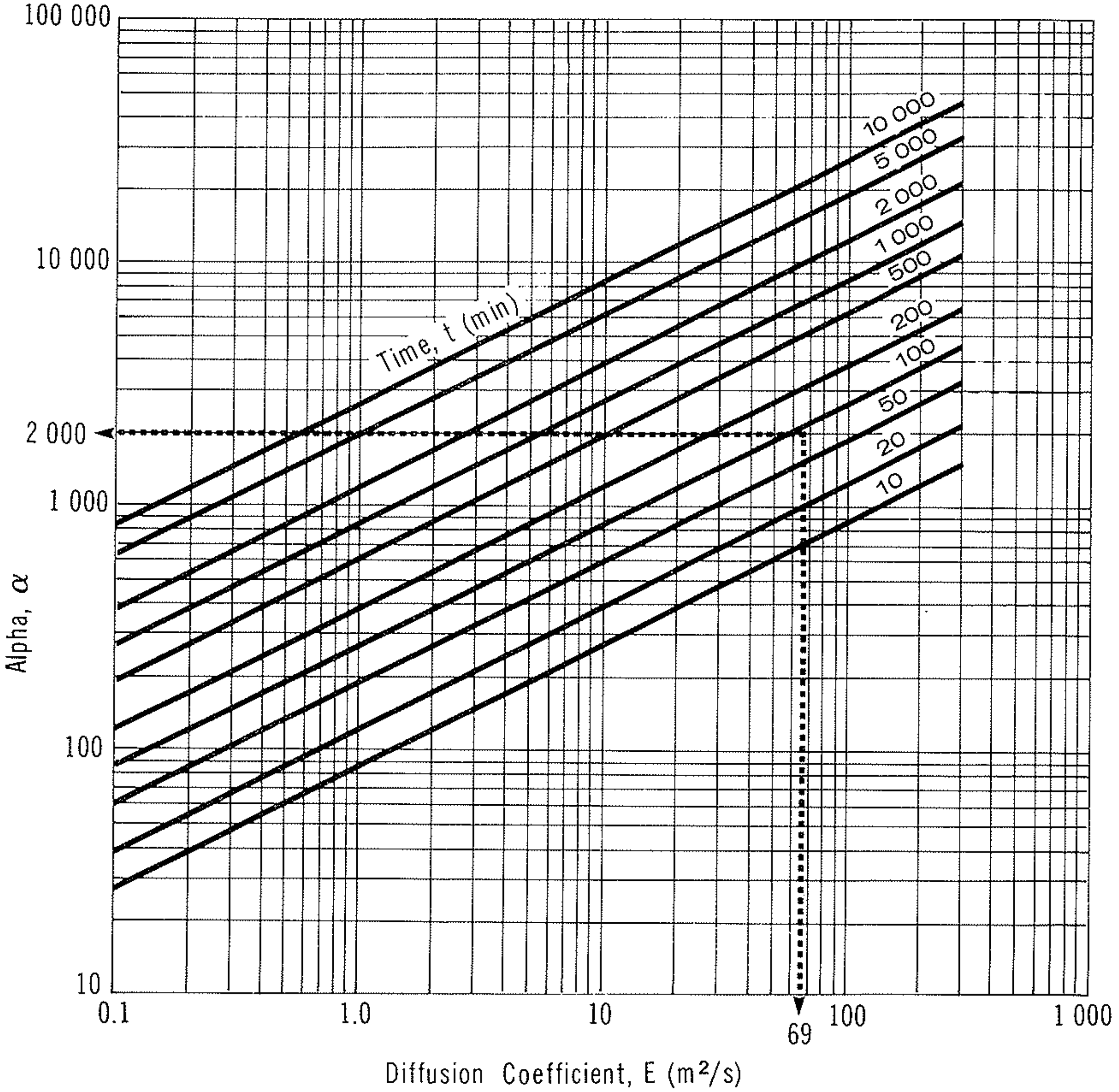
HYDRAULIC RADIUS VS CHANNEL WIDTH



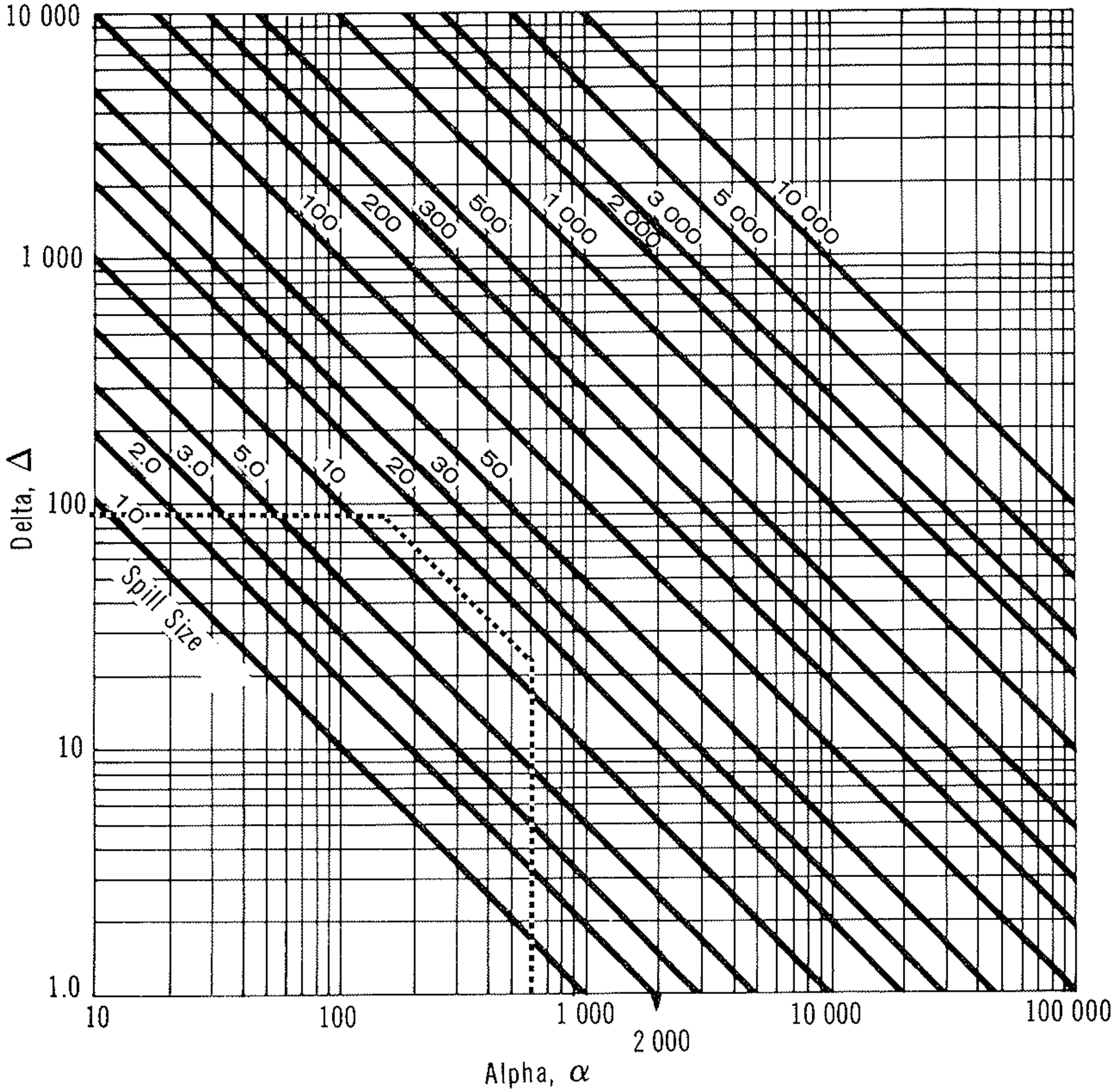
DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS



ALPHA vs DIFFUSION COEFFICIENT

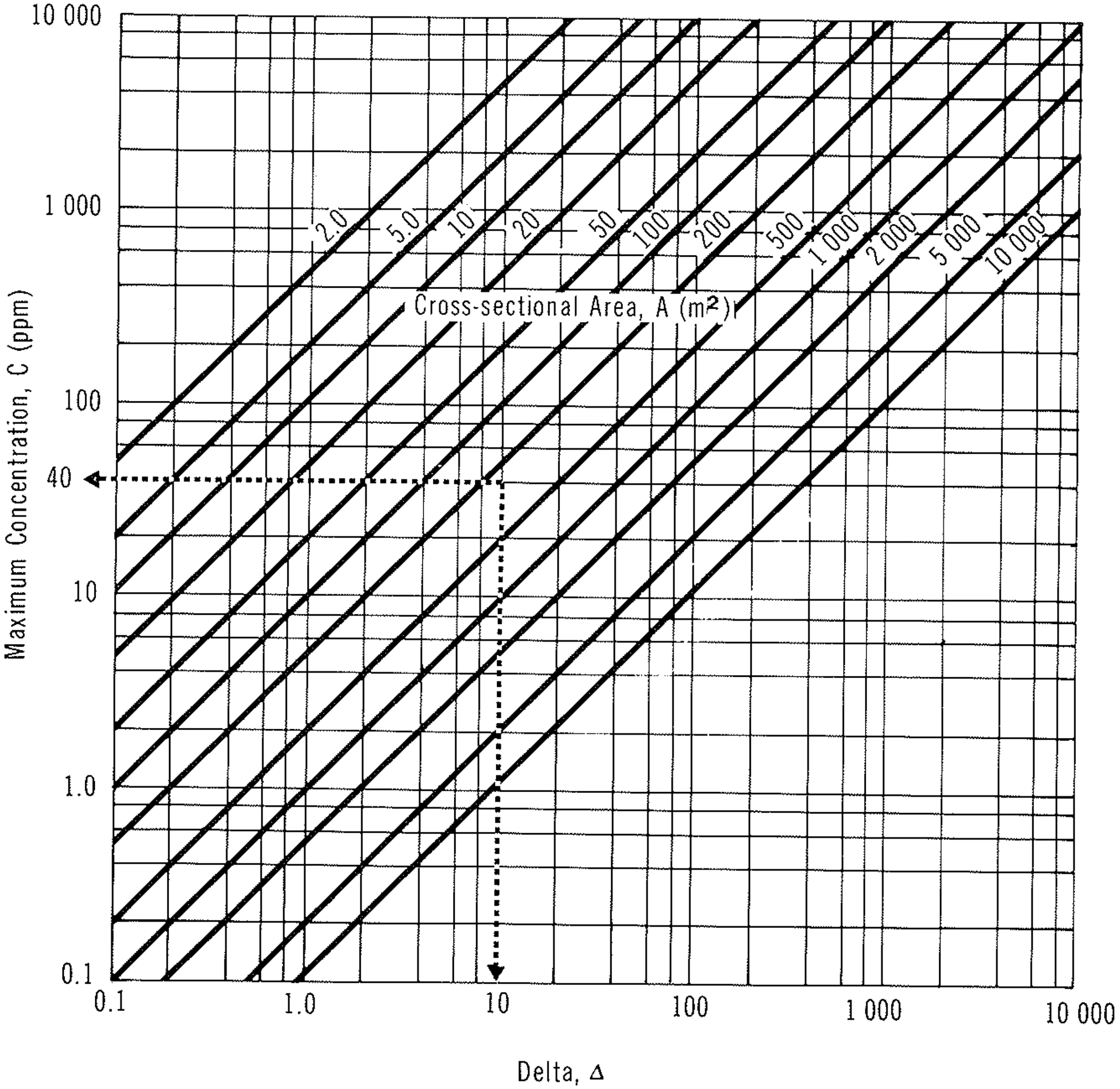


ALPHA vs DELTA



PROPYLENE OXIDE

MAXIMUM CONCENTRATION vs DELTA



(A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 28 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 29: 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 the spill. The volume of water in the cylinder can be obtained from Figure 29. The radius (r) represents the distance from the spill to the point of interest.

Figure 30: 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 30 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 propylene oxide has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

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

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

- Use Figure 23
- With X = 5000 m and U = 1 m/s, t = 83 min

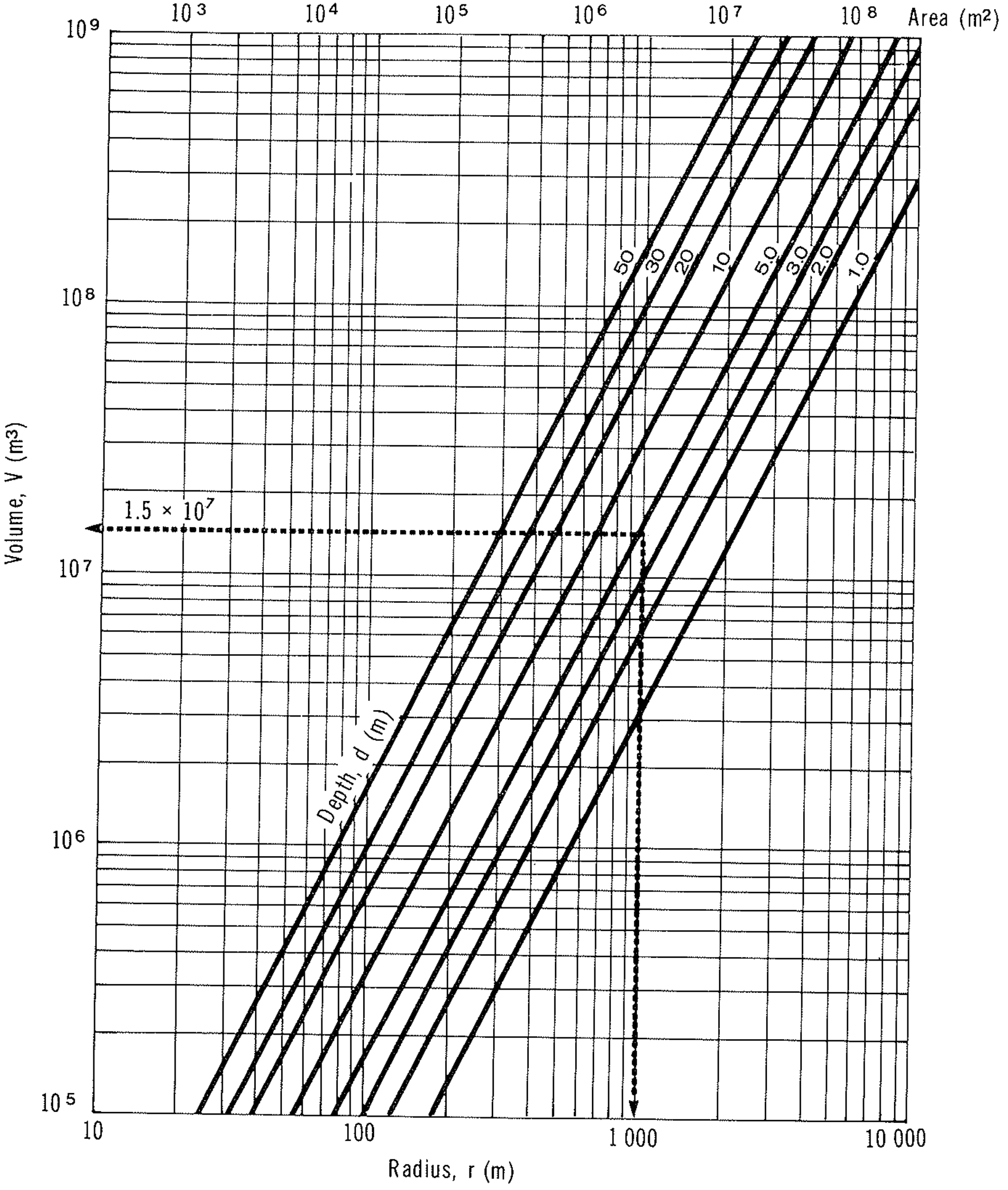
Step 3: Calculate the hydraulic radius (r)

- Use Figure 24
- With W = 50 m and U = 5 m, r = 4.2 m

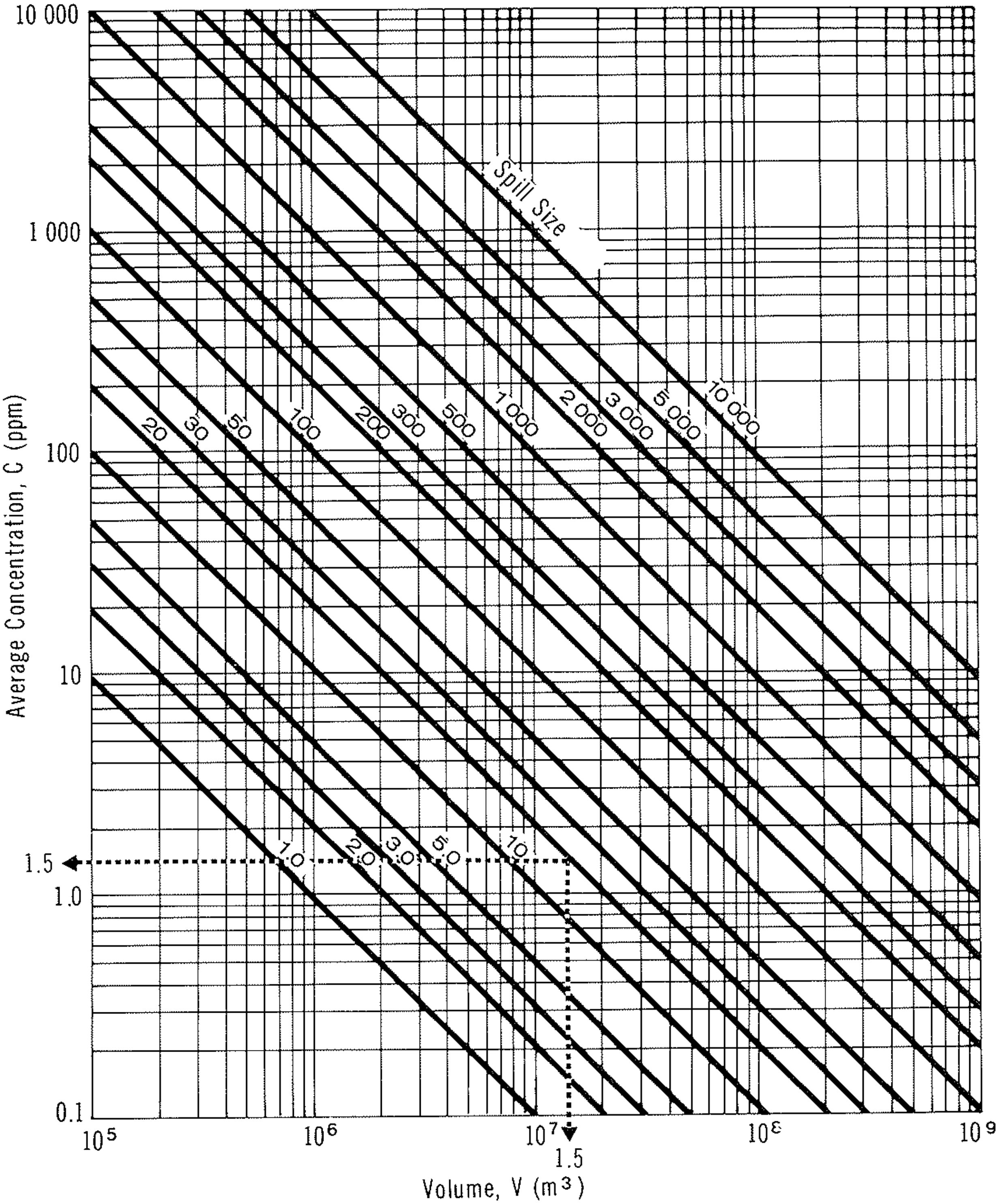
FIGURE 29

PROPYLENE OXIDE

VOLUME vs RADIUS



AVERAGE CONCENTRATION vs VOLUME



Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 25
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 26
- With E = 69 m^2/s and t = 83 min, (α) = 2000

Step 6: Calculate delta (Δ)

- Use Figure 27
- With alpha (α) = 2000 and spill mass = 20 tonnes, delta (Δ) = 10

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

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

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

- Use Figure 28
- With Δ = 10 and A = 250 m^2, C = 40 ppm

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of propylene oxide 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 (propylene oxide)

Step 2: Determine the volume of water available for dilution

- Use Figure 29
- With r = 1000 m, d = 5 m, the volume is approximately 1.5 x 10^7 m^3

Step 3: Determine the average concentration

- Use Figure 30
- With V = 1.5 X 10^7 m^3 and spill mass = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of propylene oxide onto soil and its transport downward through the soil are presented here.

Propylene oxide is a colourless liquid which mixes readily with water. When spilled onto soil, it will infiltrate and move downward into the soil. Precipitation falling at the time of the spill or water used to flush the spill site will dilute the liquid. Significant evaporation will occur from the pure liquid both while on the soil surface and also during infiltration. 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 or remain ponded.

For this work, the soils have been assumed to be at field capacity. 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, some of the propylene oxide may be attenuated by adsorption onto soil surfaces. However, most of the chemical will remain for transport down toward the groundwater table. The analysis used here neglects any retarding factors. This is shown schematically in Figure 31.

5.5.2 Equations Describing Propylene Oxide 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.

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

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

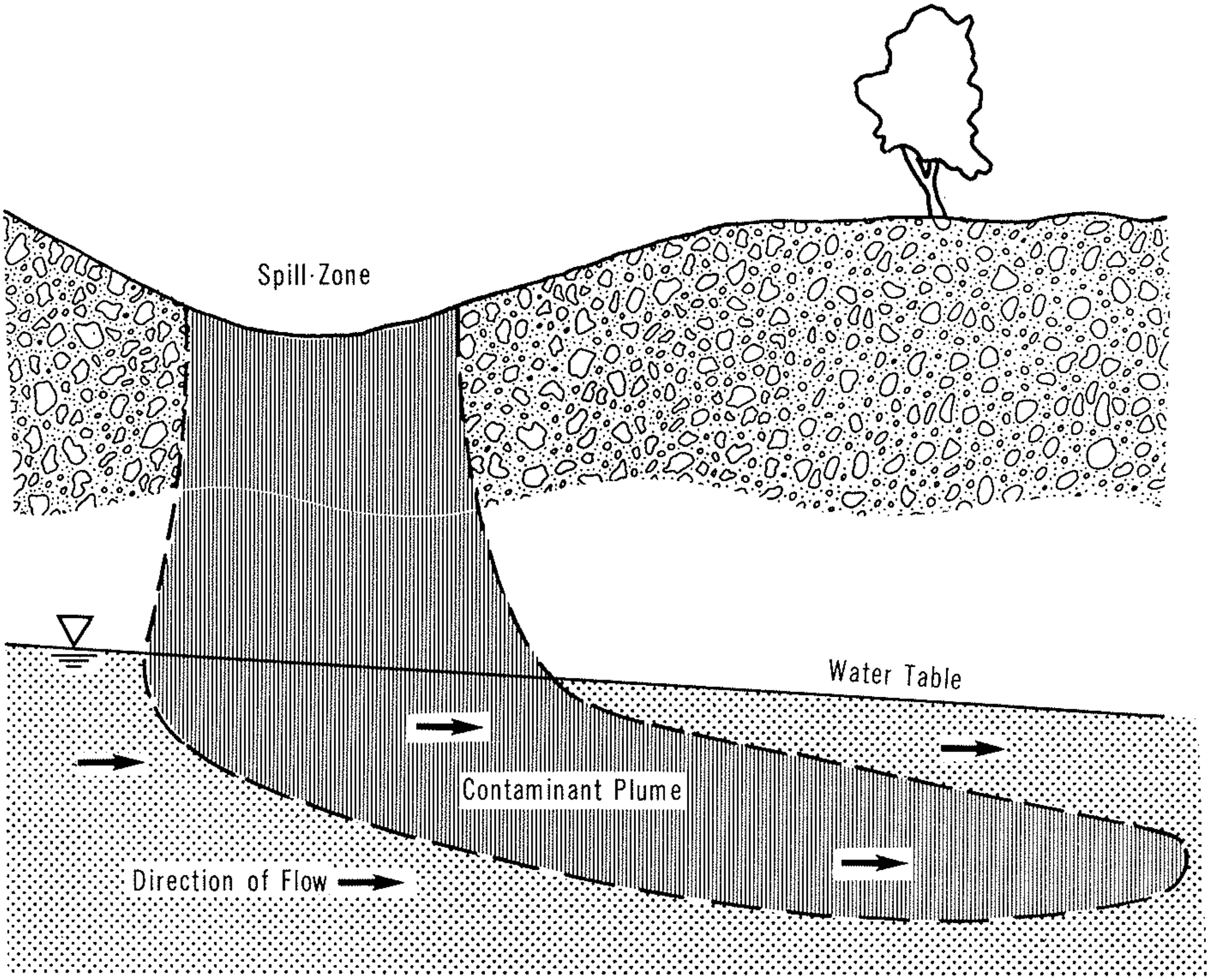
where: k = intrinsic permeability of the soil (m^2)
ρ = mass density of the fluid (kg/m^3)
μ = absolute viscosity of the fluid (Pa·s)
g = acceleration due to gravity = 9.81 m/s^2

The fluids involved are propylene oxide and water. The water calculations represent the extreme as propylene oxide is diluted. The appropriate properties for propylene oxide are given in the following chart.

FIGURE 31

PROPYLENE OXIDE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

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

–Field Capacity (θ_{fc}) = 0.075

Property	Propylene Oxide 20°C	Propylene Oxide 4°C	Water 20°C
Mass density (ρ), kg/m^3	830	840	998
Absolute viscosity (μ), Pa·s	0.31×10^{-3}	0.36×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(2.63 \times 10^7)k$	$(2.29 \times 10^7)k$	$(0.98 \times 10^7)k$

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 propylene oxide 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 32. The nomograms are presented as Figures 33, 34, and 35. 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 propylene oxide becomes diluted with water.

5.5.6 **Sample Calculation.** A 20 tonne spill of propylene oxide has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 4 minutes after the spill.

FIGURE 32

FLOWCHART FOR NOMOGRAM USE

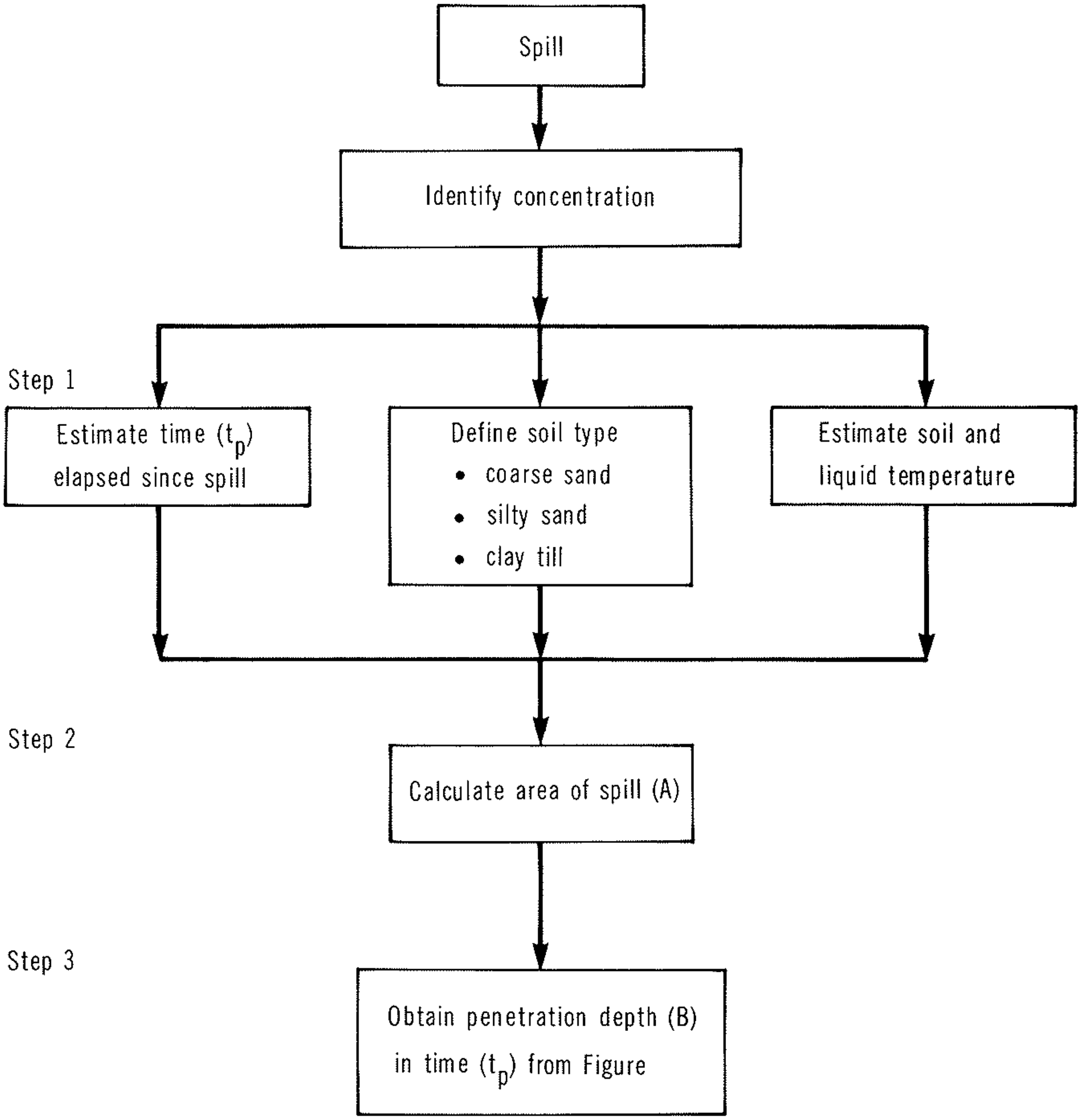
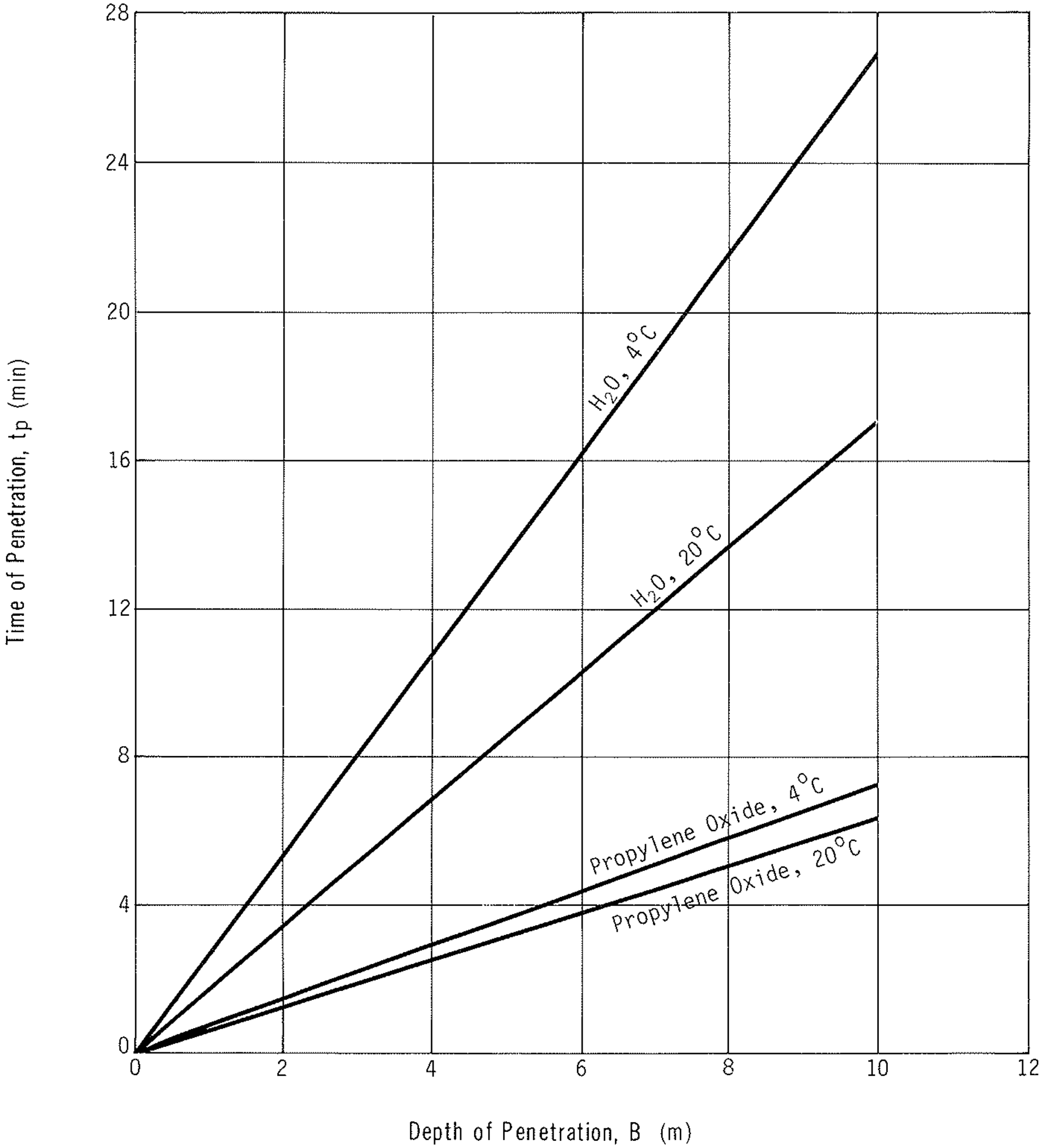


FIGURE 33

PROPYLENE OXIDE

PENETRATION IN COARSE SAND



PENETRATION IN SILTY SAND

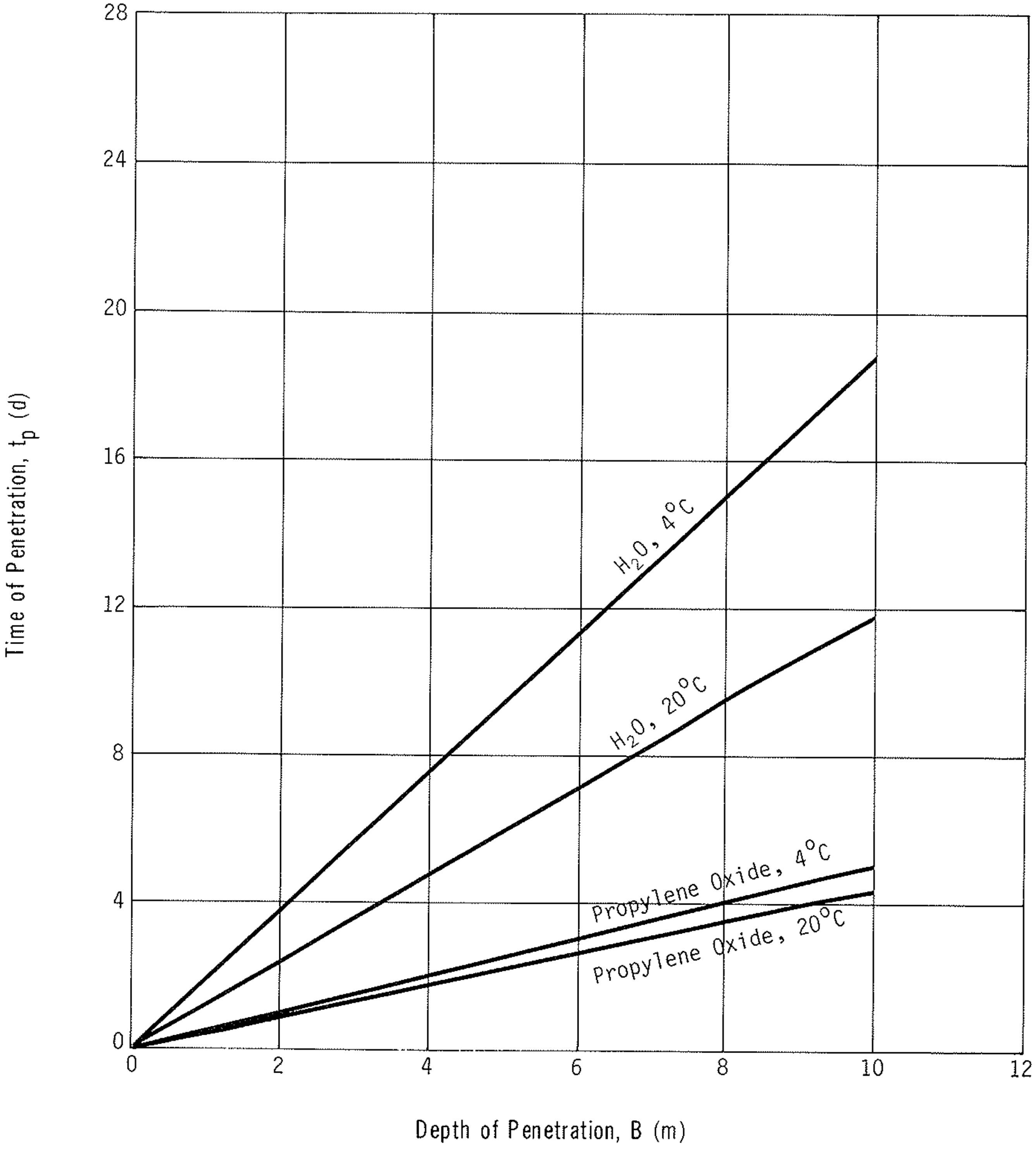
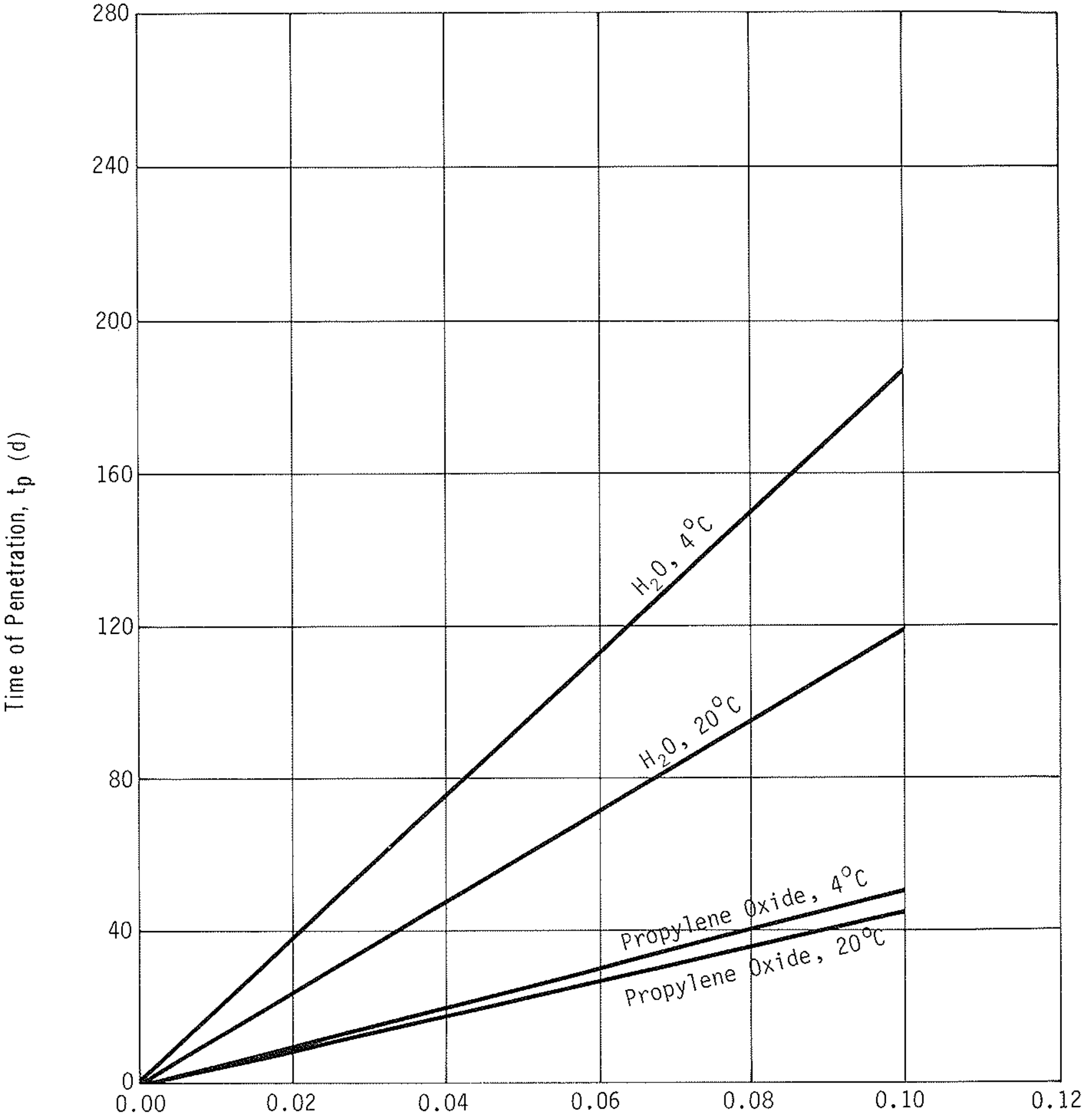


FIGURE 35

PROPYLENE OXIDE

PENETRATION IN CLAY TILL



Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- $T = 20°C$
- $r = 8.6$ m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 4 min

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 coarse sand, B = 6.2 m at $t_p = 4$ min
- Groundwater table has not been reached in this time

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Propylene oxide levels in water have not been specifically regulated in Canada or the USA.

6.1.2 Air. The environmental limit for propylene oxide in air in Ontario is 7800 $\mu g/m^3$ (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Propylene oxide has been assigned a TL_m96 of "greater than 1000 ppm" (RTECS 1979). (Note: since this assignment, lower toxicity levels have been determined.)

6.2.2 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
170	24	Goldfish	LC_{50}	static, tap water, pH 7	Bridie 1974
141	96	Mosquito fish	TL_m	static, 20°C	Verschueren 1984
215	96	Bluegill	TL_m	static, 20°C	Verschueren 1984

6.3 Mammalian Toxicology

Propylene oxide is a mild chronic irritant, moderately hazardous by all routes of absorption. The LC_{50} in air for rats is 4000 ppm for 4 hours. The LC_{50} is 1290 ppm for 14 days for skin exposure in rabbits (OHMS-TADS 1981).

6.4 Degradation

B.O.D. (W/W)	% Theo.	Days	Seed	Method	Reference
0.33	75	1/3 to 5	activated sludge	30+ days acclimation	Verschueren 1984

6.5 Long-term Fate and Effects

Propylene oxide will dissolve in water readily. In warm weather it will evaporate quickly and not persist in the aquatic environment. No bioaccumulation or concentration potential has been cited (OHM-TADS 1981).

7 HUMAN HEALTH

Propylene oxide is toxicologically classified as a primary irritant and contact with even the dilute liquid can cause skin and corneal burns. It is also a mild central nervous system depressant. The ACGIH reports that the median of the detectable odour concentrations of propylene oxide is as high as 200 ppm, considerably in excess of recommended exposure limits. Consequently, its odour cannot be used as a warning sign (Doc. TLV 1981).

Propylene oxide has been reported as a suspected animal carcinogen (RTECS 1979). In addition, considerable mutagenicity testing has been done (RTECS 1979). No information concerning propylene oxide's potential as a teratogen was found in the literature. The compound has been reported in the EPA TSCA Inventory. 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 appropriate.

7.1 Recommended Exposure Limits

The exposure standards for propylene oxide are based upon its irritant properties and its central nervous system effects. The TLV® has been set based upon propylene oxide's lesser but similar toxic effects of those of ethylene oxide (Doc. TLV 1981). Canadian provincial guidelines generally are similar to those of the USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV® (8 h)	USA-ACGIH	20 ppm (50 mg/m^3)	TLV 1983
PEL (8 h)	USA-OSHA	100 ppm (240 mg/m^3)	NIOSH/OSHA 1981
Permissible Concentration (8 h)	B.C.	100 ppm (240 mg/m^3)	B.C. 1980

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Average Exposure Criteria (TWAEC) (8 h)	Ontario	20 ppm (47 mg/m^3) (for discussion only)	Ontario 1981
Average Contamination Limit (8 h)	Saskatchewan	50 mg/m^3	Sask. 1981
Average Concentration (8 h)	Quebec	100 ppm (240 mg/m^3)	Quebec 1979
Short-term Exposure Limits (STEL)			
Permissible Concentration (15 min limit)	B.C.	150 ppm (360 mg/m^3)	B.C. 1980
Average Contamination Limit (15 min)	Saskatchewan	75 mg/m^3	Sask. 1981
Maximum Concentration	Quebec	150 ppm (360 mg/m^3)	Quebec 1979
Other Human Toxicities			
IDLH	USA-NIOSH/ OSHA	2000 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:

ITI = 1315.12 (Vapour Pressure, in mm Hg/TLV®, in ppm)

At 18°C, ITI = 1315.12 (400 mm Hg/20 ppm)

At 18°C, ITI = 2.6×10^4

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	When confined to the skin as from wearing contaminated	Patty 1981

Exposure Level (and Duration)	Effects	Reference
	clothing, the material and water solutions as dilute as 10 percent are likely to cause irritation, blistering, and even burns upon a single short exposure.	
SPECIES: Rabbit		
415 mg	On open skin caused moderate irritation.	RTECS 1979
50 mg (6 min)	Severe irritation.	RTECS 1979

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
5 mg	Severe irritation.	RTECS 1979

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristic: Sweet, ether-like odour (AAR 1981).

Odour Index: 16 600 (Verschueren 1984).

Parameter	Media	Concentration	Reference
Odour Threshold	in air	200 ppm	Doc. TLV 1981
Absolute Perception Limit	in air	9.9 ppm	Verschueren 1984
50 percent Perception Threshold	in air	35 ppm	Verschueren 1984
100 percent Perception Threshold	in air	35 ppm	Verschueren 1984

7.3.2 Taste. No data.

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
1000 ppm	Probably safe for repeated exposures (10 min/d, not more than 5/wk).	Patty 1981
1000 ppm	Probably safe for single exposure (1 h/d not more than 1/wk).	Patty 1981
400 ppm	Probably safe for repeated exposures (1 h/d, not more than 5/wk).	Patty 1981
400 ppm	Probably safe for single exposure (7 h/d not more than 1/wk).	Patty 1981
200 ppm	Probably safe for repeated exposures (4 h/d, not more than 5/wk).	Patty 1981
150 ppm	Probably safe for repeated exposures (7 h/d, not more than 5/wk).	Patty 1981
SPECIES: Dog		
2480 ppm (4 h)	3/3 died within hours.	Patty 1981
2005 ppm (4 h)	LC_{LO}	RTECS 1979
1330 ppm (Unspecified duration)	0/3 died in 14 days.	Patty 1981
SPECIES: Guinea Pig		
14 400 ppm (1 h)	5/5 died.	Patty 1981
14 400 ppm (Unspecified duration)	0/5 died.	Patty 1981
7200 ppm (Unspecified duration)	0/10 died.	Patty 1981
4000 ppm (4 h)	LC_{LO}	RTECS 1979
3600 ppm (2 h)	0/5 died.	Patty 1981
3600 ppm (5 h)	1/5 died.	Patty 1981
3600 ppm (7 h)	2/5 died.	Patty 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
14 400 ppm (0.5 h)	Fatal in 10/10 cases.	Verschueren 1984
7200 ppm (1 h)	Fatal in 5/10 cases.	Verschueren 1984
4000 ppm (4 h)	LC_{LO}	RTECS 1979
3600 ppm (1 h)	0/5 died. No detectable injuries were noted.	Patty 1981
3600 ppm (2 h)	4/10 died.	Patty 1981
SPECIES: Mouse		
1330 ppm (4 h)	1/10 died.	Patty 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Swallowing is unlikely. Would cause irritation and burns of mouth and gastrointestinal tract. May cause nausea and vomiting.	AAR 1981
SPECIES: Guinea Pig		
690 mg/kg	LD_{50}	RTECS 1979
SPECIES: Rat		
930 mg/kg	LD_{50}	RTECS 1979

7.4.3 Skin Contact (Systemic Effects).

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Rabbit		
1500 mg/kg	LD_{50}	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
SPECIES: Guinea Pig		
8640 mg/kg	LD_{50}	RTECS 1979

7.4.4 Mutagenicity, Teratogenicity and Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
1850 µg/L (1 h)	Cytogenic analysis using human leukocytes. No results reported.	RTECS 1979
SPECIES: Mouse		
3640 mg/kg (91 wk, intermittently	Neoplasm formation on subcutaneous administration.	RTECS 1979
SPECIES: *Salmonella typhimurium*		
700 µg/plate	Mutation in microorganism testing to detect heritable genetic alterations.	RTECS 1979
700 µg/plate	Microsomal mutagenicity assay to determine induced mutation frequencies.	RTECS 1979
SPECIES: *Escherichia coli*		
700 µg/plate	Mutation in microorganism testing to detect heritable genetic alterations.	RTECS 1979
700 µg/plate	Microsomal mutagenicity assay to determine induced mutation frequencies.	RTECS 1979

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 eyes, nose, throat and lungs.

2. Headache.
3. Nausea.
4. Vomiting.
5. Ataxia.
6. Mild central nervous system depression.
7. Loss of consciousness (CHRIS 1978).

7.5.2 Ingestion.

1. Irritation or burns of mouth and gastrointestinal tract (NIOSH/OSHA 1981).
2. Nausea.
3. Vomiting.

7.5.3 Skin Contact.

1. Irritation.
2. Blistering (Patty 1981).
3. Burns.
4. Corrosion.

7.5.4 Eye Contact.

1. Irritation.
2. Corneal burns.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Propylene Oxide with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Fire		●	●										Flammable liquid. Vapours form explosive mixtures with air.	Sax 1979; NFPA 1978
Heat		●	●										Flammable liquid. Vapours form explosive mixtures with air.	Sax 1979
SPECIFIC CHEMICALS														
Ammonium Hydroxide	●								●				With 28 percent ammonium hydroxide.	NFPA 1978
Chlorosulphonic Acid	●								●					NFPA 1978
Hydrochloric Acid	●								●					NFPA 1978
Hydrofluoric Acid	●								●				With 48.7 percent HF.	NFPA 1978
Nitric Acid	●								●				With 70 percent HNO_3.	NFPA 1978
Oleum	●								●					NFPA 1978
Sodium Hydroxide		●	●			●							Polymerization probably occurred.	Bretherick 1979

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

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Sulphuric Acid	●								●				With 96 percent H_2SO_4.	NFPA 1978
CHEMICAL GROUPS														
Catalytic Compounds					●								e.g., Anhydrous chlorides of iron, tin, aluminum, etc.	CCPA 1984
Explosives			●											EPA 600/2-80-076
Oxidizing Agents	●	●											Exhaustive oxidation.	EPA 600/2-80-076
Reducing Agents	●													EPA 600/2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a 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. Countermeasures are dependent on the situation; therefore, 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. Propylene oxide is a flammable liquid. Its vapours form explosive mixtures with air. Vapour may travel considerable distance to a source of ignition and flash back. Propylene oxide may polymerize with evolution of heat when in contact with highly active catalytic surfaces such as anhydrous chlorides of iron, tin and aluminum, peroxides of iron and aluminum, strong acids and alkali metal hydroxides. If the polymerization takes place in a container, there is possibility of violent rupture of the container (NFPA 1978).

9.1.2 Fire Extinguishing Agents. Use water spray at a safe distance to cool containers involved in a fire to prevent rupture (ERG 1980). Do not extinguish fire until leak can be stopped (CCPA 1984). Water may be ineffective in some circumstances (Kirk-Othmer 1982).

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

Move containers from fire area if this can be done without risk. Stay away from tank ends. For massive fires, use unmanned hose holder or monitor nozzles (ERG 1980).

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

Toxic Vapour Hazard: 335 m downwind by 180 m wide
Explosion Hazard: 1520 m radius

9.1.4 Spill Actions.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (Dow ERIS 1981). Use water spray or foam to reduce vapours and to protect men effecting the shut-off (NFPA 1978; FCHHS 1981).

9.1.4.2 Spills on land. For small spills, adsorb on inert, noncombustible sorbent material such as sand or vermiculite and shovel into steel containers for disposal (FCHHS 1981; CCPA 1984).

For large spills, contain if possible by forming a mechanical barrier to prevent spreading. Remove as much material as possible using vacuum equipment and pumps. Clean up the remainder with sorbents such as sand or vermiculite.

9.1.5 Cleanup and Treatment.

9.1.5.1 Spills in/on water. If possible, contain the contaminated water and remove for biological treatment such as at a sewage plant. Carbon treatment in-situ or otherwise is not effective. It is reported that propylene is absorbed at a ratio of 0.052 g per g of carbon with 26.1 percent efficiency when 1000 mg/L influent was applied (effluent was 739 mg/L) (Verschueren 1984).

9.1.5.2 General. Propylene oxide in low concentrations can be biologically treated if a suitable facility is available (Arco MSDS 1981).

9.1.6 Disposal. Waste propylene oxide must never be discharged directly into sewers or surface waters. It may be burned in an approved incinerator with an additional solvent to assist burning, or it can be treated at an approved waste management facility.

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

If the spilled material is known to be propylene oxide:

- Polyethylene is penetrated by propylene oxide in about 1 hour. The following clothing materials are penetrated in less than 1 hour: natural rubber, neoprene, nitrile, polyurethane, polyvinyl alcohol and polyvinyl chloride (Little 1983).
- 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 skin contact with liquid propylene oxide (NIOSH/OSHA 1981).

- Chemical safety goggles should also be worn where splashing or spraying in the eyes may occur (Arco MSDS 1981).
- Gloves made of polyethylene, EPDM or butyl rubber are recommended (FCHHS 1981).
- Nonimpervious clothing which becomes contaminated with liquid propylene oxide or any clothing which becomes wet with liquid propylene oxide should be removed immediately and such clothing should not be reworn until the propylene oxide 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 (NIOSH/OSHA 1981).
- The following is a list of the minimum respiratory protection recommended for personnel working in areas where propylene oxide is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapour Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapour cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapour canister.
2000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 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.

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapours.
	Any escape self-contained breathing apparatus.

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

** Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of propylene oxide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 2000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

9.1.8 Storage Precautions. Protect containers against physical damage. Detached outside storage is preferred. Inside storage should be in a standard flammable liquids storage room or cabinet. Isolate from combustible materials and from oxidizing materials (NFPA 1978). Propylene oxide should not be stored in the presence of acids, bases, chlorides of iron, aluminum and tin, or peroxides of iron and aluminum. Any of these may cause violent polymerization (Kirk-Othmer 1982).

Propylene oxide will attack some forms of plastics, rubber, and coatings. No acetylide-forming metals such as copper or copper alloys should be in contact with propylene oxide (NIOSH/OSHA 1981).

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experiences 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 problem 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. In the case of propylene oxide, a well-documented and useful illustration could not be found.

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 Propylene Oxide in Air

11.1.1 Gas Chromatography (NIOSH 1977). A range of 121 to 482 mg/m^3 (50-203 ppm) of propylene oxide in air may be determined by gas chromatography.

A known volume of air is drawn through a 7 cm x 6 mm O.D. charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 3 mm portion of urethane foam. The first section contains 100 mg, whereas the second section contains 50 mg. A silylated glass wool plug is placed before the front absorbing section. A sample size of 5 L at a flow of 200 mL/min is recommended.

The charcoal tube sample is scored before the first section of charcoal and broken. The larger charcoal section is transferred to a 1 mL stoppered sample container containing 0.5 mL of carbon disulphide. The same operation is performed with the back-up section. The sample should be allowed to desorb for 30 minutes. A 5 µL aliquot of sample is injected into a suitable gas chromatograph equipped with a flame ionization detector.

The sample is determined using a suitable electronic integrator which measures peak area. The concentration is measured using a calibration curve. Typical gas chromatograph operating 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 190°C, detector temperature at 255°C, column temperature at 145°C, and a 122 x 0.6 cm (4 ft. by 1/4 in.) stainless steel column packed with 50/80 mesh Porapak, Type Q.

11.2 Qualitative Method for the Detection of Propylene Oxide in Air

A range of 50 to 3000 ppm of propylene oxide in air may be determined with the use of a Drager detector tube for ethylene oxide. The ethylene oxide tubes are used for propylene oxide although they have a different sensitivity. A known volume of air is drawn through a Drager detector tube for ethylene oxide using a Drager gas detector tube pump. A colour change of the pale yellow indicating layer to pale turquoise green indicates propylene oxide. This is based on the reaction of propylene oxide with a chromium VI compound to form a chromium III compound (Drager 1979).

11.3 Quantitative Method for the Detection of Propylene Oxide in Water

11.3.1 Partition Infrared (AWWA 1981). A range of 40 to 400 ppm of propylene oxide in water may be determined using partition infrared spectrophotometry.

A minimum volume of 1 L of representative sample is collected in an appropriate container and acidified to pH 2 with dilute hydrochloric acid. A 5 mL volume of acid should be sufficient.

The sample is transferred to a separatory funnel and a 30 mL volume of Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is added after it is used to rinse the sample container. The solvent layer is drained into a 100 mL volumetric flask. Two more 30 mL Freon® extractions are carried out and the extracts combined in the 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon®. The sample is scanned on a suitable infrared spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells. The sample concentration is determined from a calibration curve.

11.4 Qualitative Method of the Detection of Propylene Oxide in Water

The sample is collected as in Section 11.3.1 and extracted with Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane). The sample is scanned on a suitable double-beam recording spectrophotometer using matched 1 cm cells with Freon® in the reference cell. The presence of characateristic absorbance bands on the chromatogram indicates propylene oxide (AWWA 1981).

11.5 Quantitative Method for the Detection of Propylene Oxide in Soil

11.5.1 Partition Infrared (AWWA 1981). Concentrations greater than 40 ppm of propylene oxide in soil may be determined by 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 propylene oxide. Three extractions using 30 mL of 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 to 2700 cm^{-1} using matched 1 cm rear infrared silica cells. The sample concentration is determined from a calibration curve.

11.6 Qualitative Method for the Detection of Propylene Oxide in Soil

The sample is collected as in Section 11.5.1 and extracted using Freon 113®. The sample is scanned on a suitable double-beam recording infrared spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells and Freon® in the reference cell. The presence of characteristic absorbance bands on the chromatogram indicates the presence of propylene oxide (AWWA 1981).

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Common Abbreviations

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