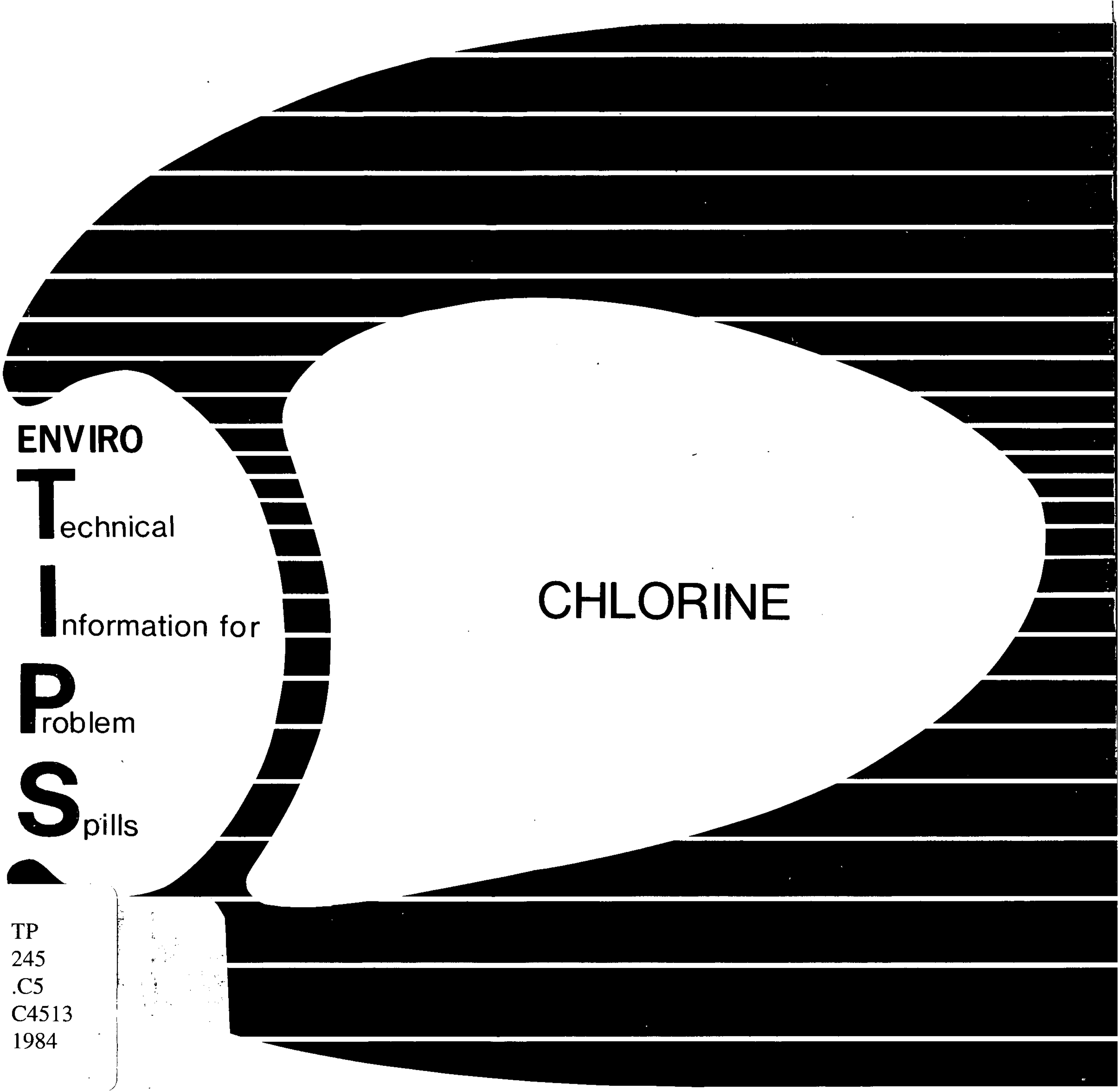
Environment Canada
Environmental Protection Service

Environnement Canada
Service de la protection de l'environnement



ENVIRO
Technical Information for Problem Spills

CHLORINE

March 1984

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 the impact on the environment. The manual 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.

CHLORINE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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

March 1984

Cat. No. En 48-10/6-1984E
ISBN 0-662-13179-7
BEAUREGARD PRESS LIMITED

FOREWORD

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

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who 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

CHLORINE (Cl_2)

Greenish-yellow gas with an irritating, bleach-like odour

SYNONYMS

Chlore (Fr.)

IDENTIFICATION NUMBERS

UN. No. 1017; CAS No. 7782-50-5; OHM-TADS No. 7216637; STCC No. 4904120

GRADES & PURITIES

99.5 to 100 percent

IMMEDIATE CONCERNS

Fire: Non-combustible. Combines with water or steam to produce toxic and corrosive fumes of HCl. Will support combustion

Human Health: Highly toxic via all routes

Environment: Highly toxic to aquatic life. Harmful to some species of aquatic life at concentrations as low as 0.1 mg/L. Chlorine gas is highly toxic to plants and animals

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): gas
Shipping state: liquified gas
Boiling Point: -34.6°C
Melting Point: -100.98°C
Flammability: noncombustible
Vapour Pressure: 759.1 kPa @ 25°C; 589.2 kPa @ 21°C
Density: (liquified Cl): 1.46 kg/L @ 0°C; (dry gas): 3.21 g/L @ std. conditions
Solubility (in water): 0.73 g/100 mL @ 20°C
Behaviour (in water): liquid sinks and boils, forms chlorine hydrate ($Cl_2 \cdot H_2O$) and a corrosive solution (HCl and Cl_2 dissolved in water)
Behaviour (in air): gas hugs the ground
Odour Threshold: 0.3 to 5 ppm
Vapour Density (air = 1): 2.48 (dry gas, std. cond.)

ENVIRONMENTAL CONCERNS

Chlorine is highly toxic to all forms of aquatic life. There is no potential for bioaccumulation or bioconcentration.

HUMAN HEALTH

TLV®: 1 ppm (3 mg/m^3)

IDLH: 25 ppm

Exposure Effects

Inhalation: Extremely irritating to respiratory tract within a few minutes of inhalation

Contact: Any contact with liquid chlorine causes local irritation, severe burns, blistering and tissue destruction. Contact to eyes causes burning, watering and possible loss of sight

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE; POISON". Call fire department and notify manufacturer. Stop leak or flow of gas and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Vapour cloud collects in low-lying areas. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not combustible, but will support combustion. Use foam, dry chemical or carbon dioxide to extinguish fire in vicinity. Wear full protective clothing and SCBA. Cool fire-exposed containers with water spray. Stay clear of ends of tanks. Do not apply water directly to leak or inside containers. Some fires involving chlorine may only be extinguished by stopping flow of gas.

COUNTERMEASURES

Emergency Control Procedures in/on

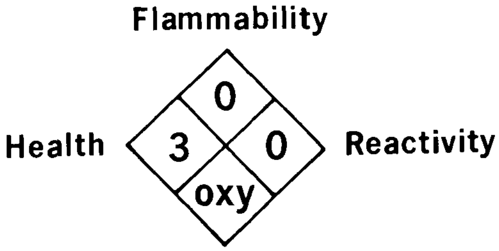
Soil/Water: Construct barriers to contain spill or divert to impermeable surfaces. Special foams may be used to minimize vaporization. Special kits can be used to seal leaking container. Do not put water on leaking container or on liquid spills. Neutralize spilled liquids.

Air: Use water spray to knock down and disperse vapour. Control runoff for later treatment and/or disposal.

NAS HAZARD RATING

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

NFPA
HAZARD
CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Greenish yellow gas. Liquid chlorine has a clear amber colour (CIL TSB)
Usual shipping state	Liquid (compressed and liquified gas) (HCG 1981)
Physical state at 15°C, 1 atm	Gas
Melting point	-100.98°C (Dow CH 1966)
Boiling point	-34.6°C (CRC 1980)
Vapour pressure	759.1 kPa (25°C) (Chem. Eng. 1974) 589.2 kPa (21°C) (HCG 1981)

Densities

Density (liquid) (saturated gas)	1,468.4 g/L (0°C) (Kapoor 1957) 12.07 g/L (0°C, 3.66×10^5 Pa) (CM 1976)
Specific gravity	1.468 (0°C) (HCG 1981)
Vapour density	3.209 g/L (std. cond.) (dry gas) (Kapoor 1957) 2.482 (specific gravity 0°C) (dry gas) (Meinhardt 1981)

Fire Properties

Flammability	Noncombustible in air (NFPA 1978). Capable of supporting the combustion of certain substances (HCG 1981)
Behaviour in a fire	Capable of supporting combustion of certain substances (HCG 1981)

Other Properties

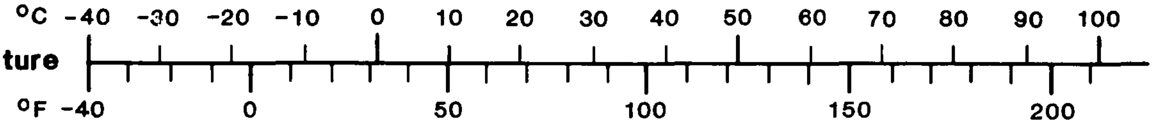
Molecular weight of pure substance	70.906 (CRC 1980)
Constituent components of typical commercial grade	$\geq$ 99.5% Cl_2 $\leq$ 0.5% gaseous, liquid and solid impurities (Hooker PIM 1979)
Reactivity index	$> 10^{14}$ ohm·m (70°C) (MCA 1970)
Refractive index	1.000768 (gas) (CRC 1980) 1.367 (liquid) (CRC 1980)

Viscosity	0.014 mPa·s (gas at 20°C) (Dow CH 1966) 0.35 mPa·s (liquid at 20°C) (Dow CH 1966)
Liquid surface tension	25.4 mN/m (liquid at -29°C) (CRC 1980)
Latent heat of fusion	90.39 kJ/kg (-100.98°C) (HCG 1981)
Latent heat of sublimation	382.8 J/g (25°C) (Perry 1973)
Latent heat of vaporization	287.8 kJ/kg (-34.05°C) (HCG 1981)
Ionization potential	11.48 eV (Rosenstock 1977)
Heat capacity	
constant pressure (C_p)	0.473 kJ/kg·°C (HCG 1981)
constant volume (C_v)	0.348 kJ/kg·°C (HCG 1981)
C_p/C_v	1.355 (CM 1970)
Critical pressure	7,711.1 kPa (HCG 1981)
Critical temperature	144°C (Dow CH 1966)
Coefficient of thermal expansion (0-100°C)	3.8×10^{-3}/°C (Perry 1973)
Liquid-gas volume relationship	457.6 (std. cond.) (CM 1976)
Thermal conductivity	8.82×10^{-3} watt/mik (27°C) (CRC 1980)
Saturation concentration (calc.)	882.3 g/m^3 (-7°C) (CRC 1980)
Diffusivity	1.44×10^{-5} cm^2/s (in water 25°C) (Perry 1973)
Solubility	
in water	0.73 g/100 g (20°C) (Dow MSDS 1979)
Vapour Weight to Volume Conversion Factor	1 ppm = 2.951 mg/m^3 (20°C) (Verschueren 1977)

TABLE 1

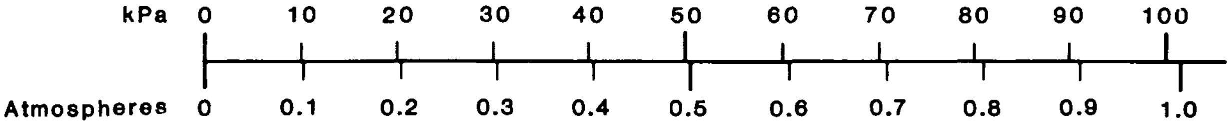
CONVERSION NOMOGRAMS

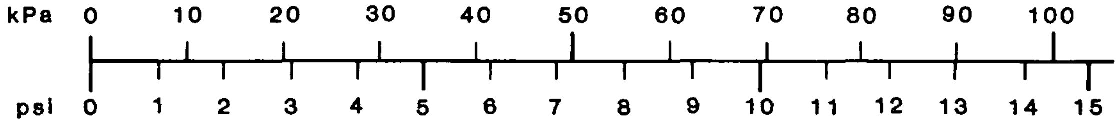
Temperature

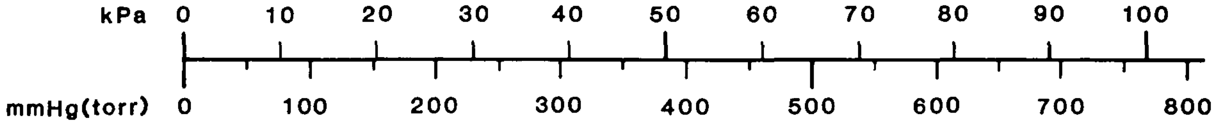


Pressure

1 kPa = 1,000 Pa







Viscosity

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

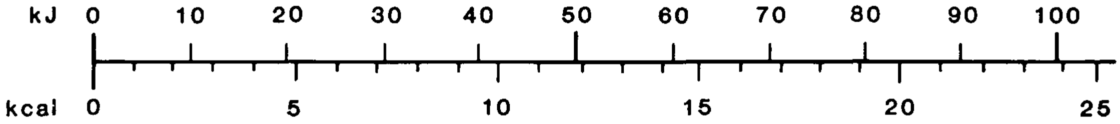
Kinematic 1 m^2/s = 1,000,000 centistokes (cSt)

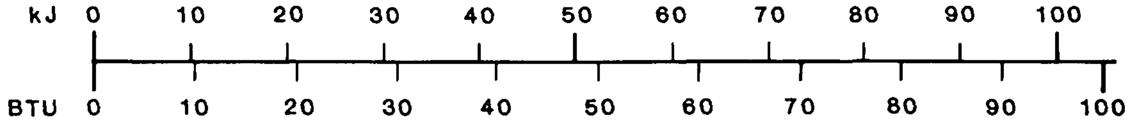
Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat)

1 kJ = 1,000 J





Density

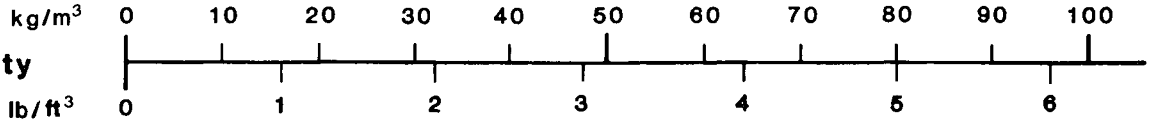


FIGURE 1

CHLORINE

VAPOUR PRESSURE VS TEMPERATURE

Reference: Chem. Eng. 1974

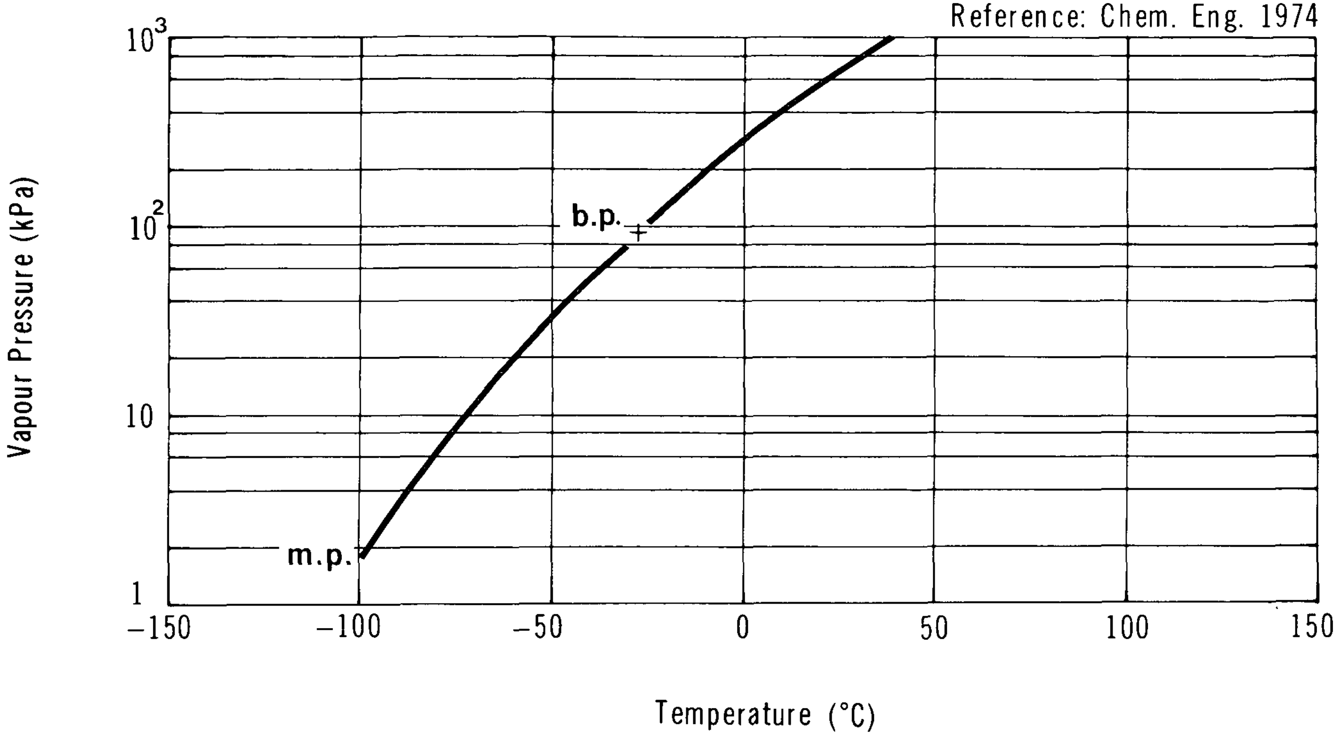


FIGURE 2

CHLORINE

LIQUID DENSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

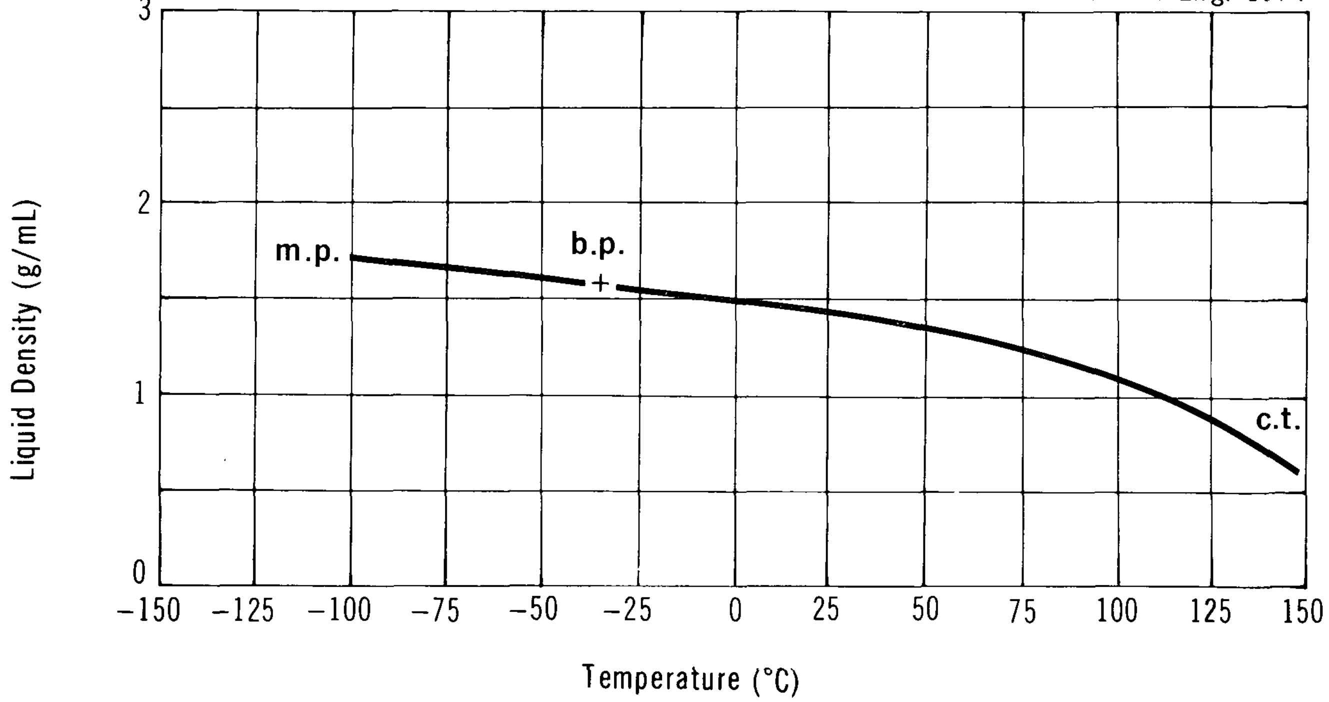


FIGURE 3

CHLORINE

LIQUID VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

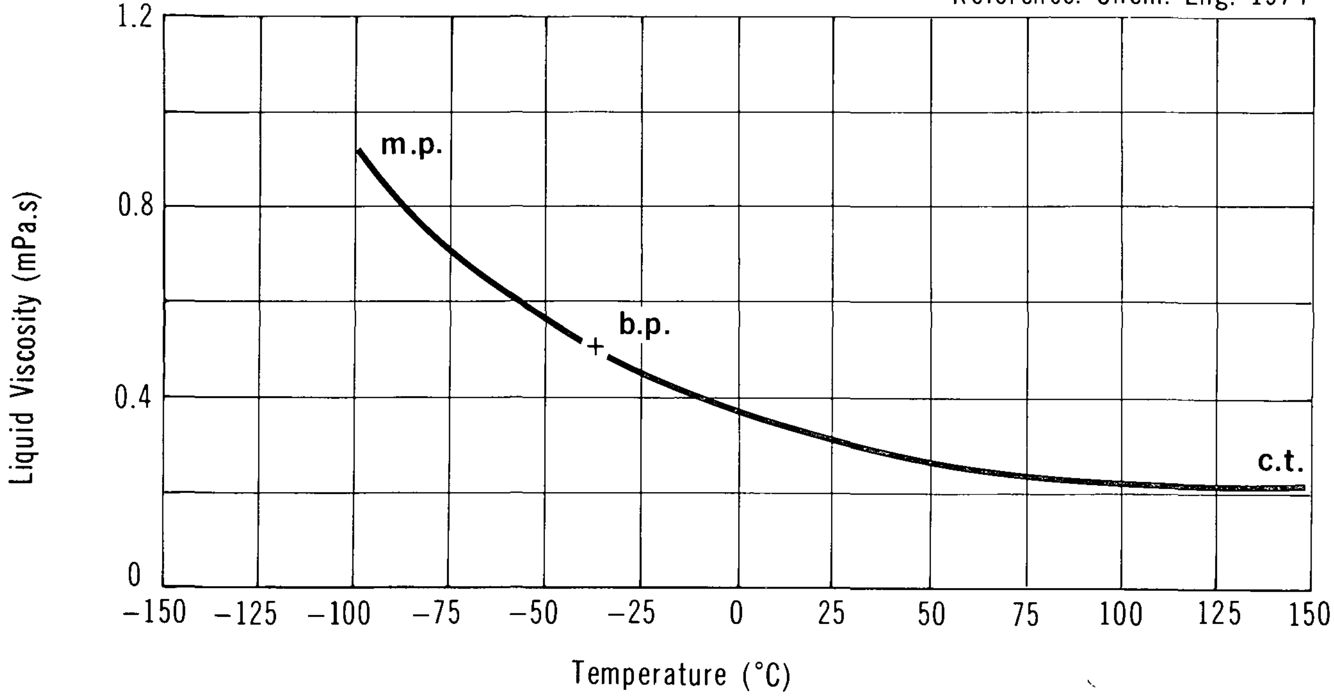


FIGURE 4

CHLORINE

VAPOUR VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

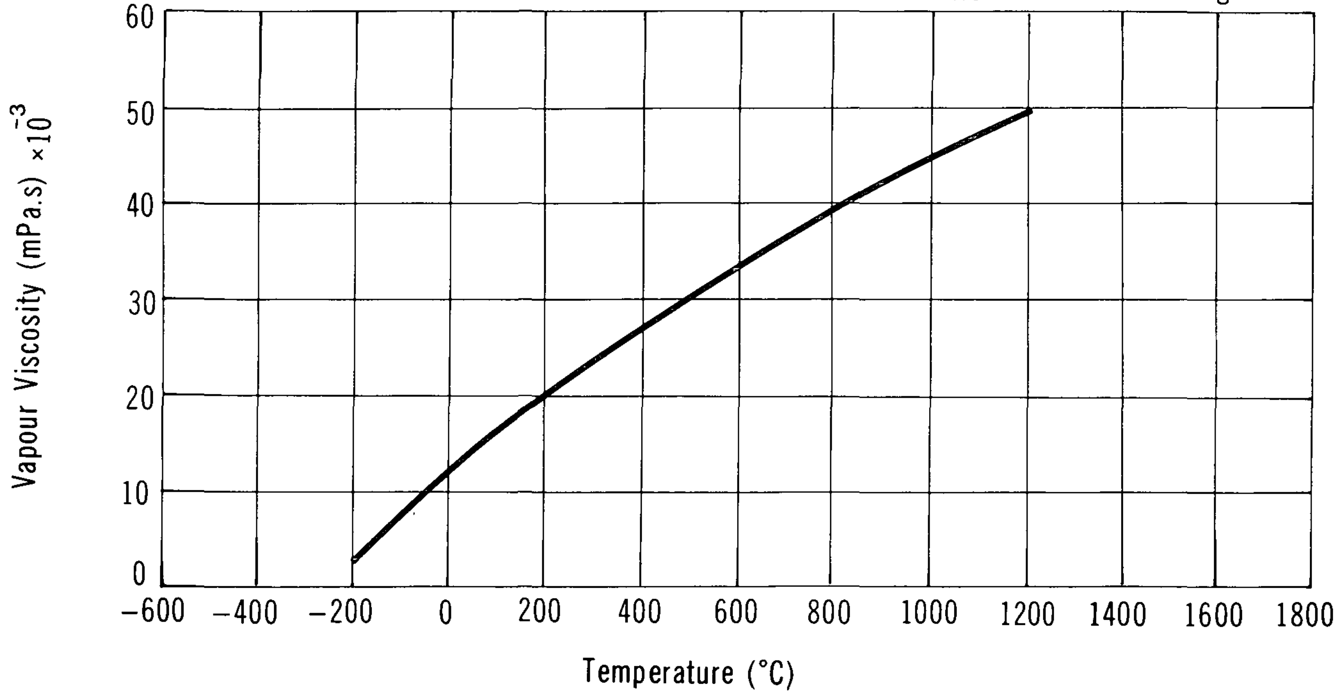


FIGURE 5

CHLORINE

SOLUBILITY IN WATER vs TEMPERATURE

Reference: Dow CH

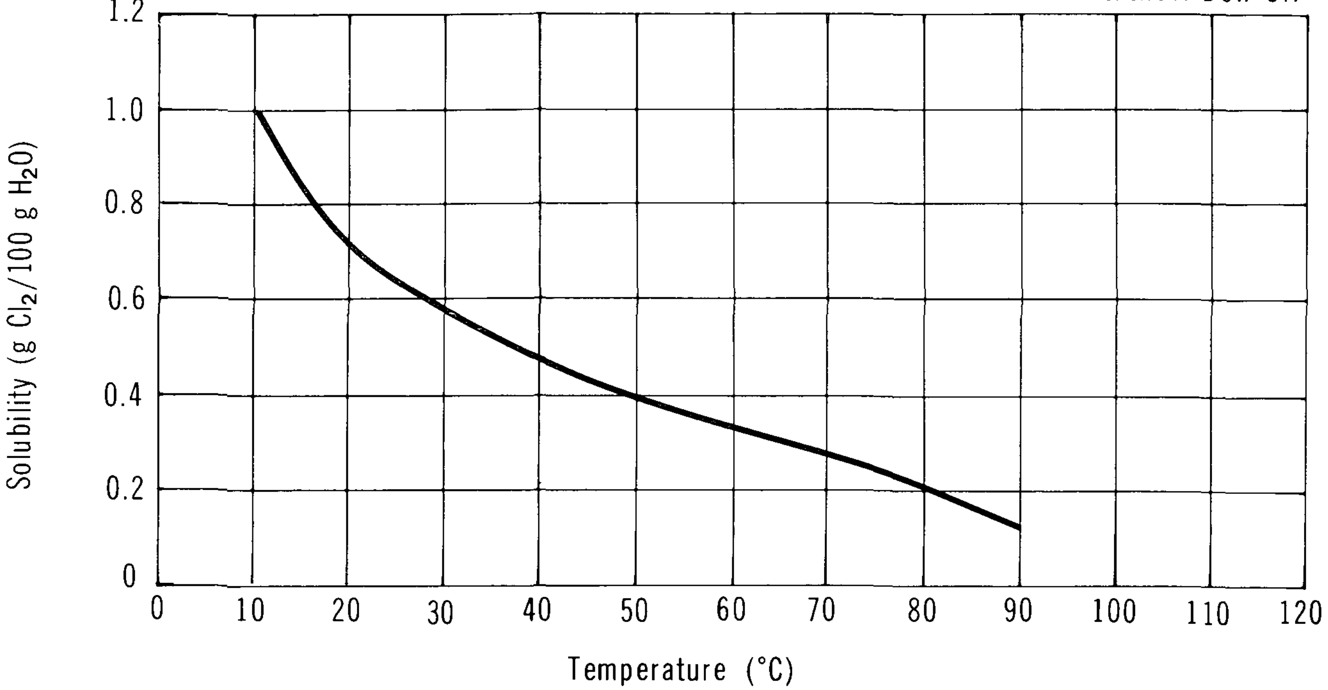
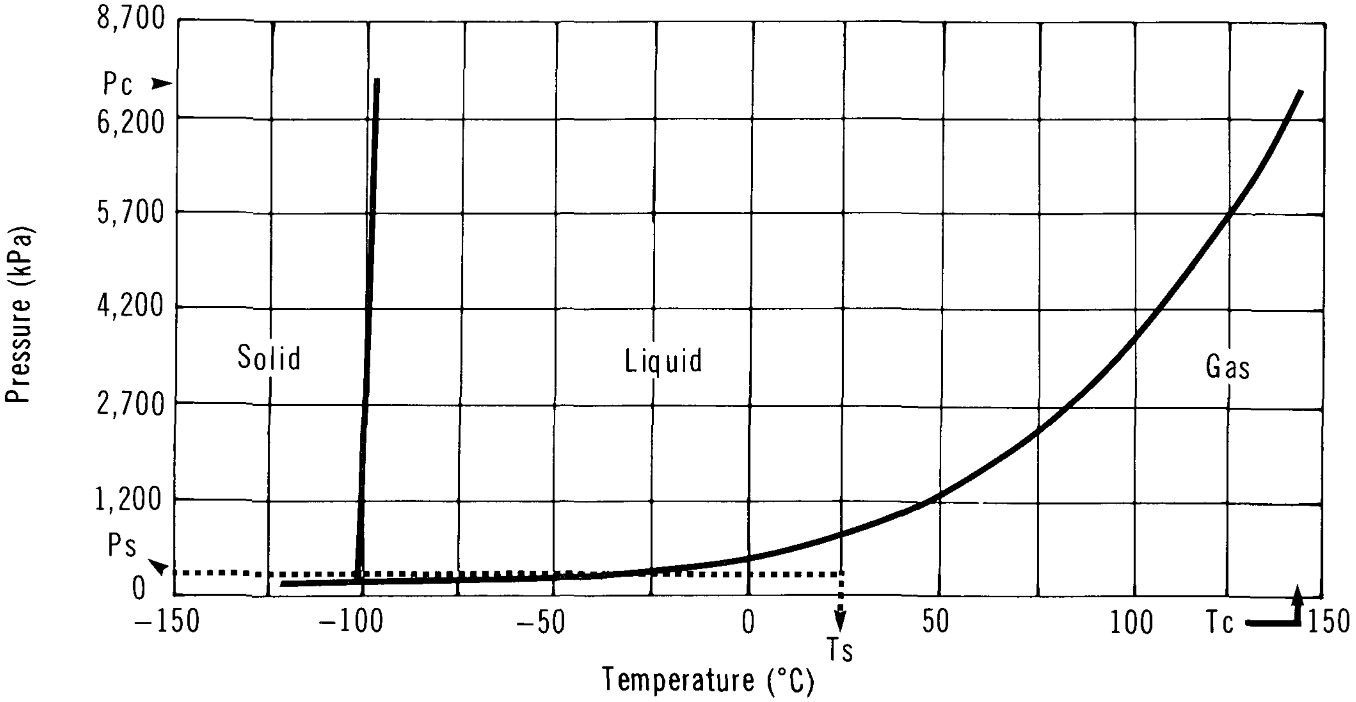


FIGURE 6

CHLORINE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Dow MSDS 1979; Hooker PIM 1979; CIL TSB)

Chlorine is shipped as a liquified compressed gas with a minimum of 99.5 percent purity.

3.2 Domestic Manufacturers (Corpus 1981; Scott 1979; CCPA 1981)

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

CIL Inc.
45 Sheppard Avenue East
Willowdale, Ontario
M2N 5W9
(416) 226-6110

Canadian Occidental Petroleum Limited
Hooker Chemical Division
700 Fourth Avenue S.W.
Calgary, Alberta
T2P 0K2
(403) 265-2390

Canso Chemicals Limited
P.O. Box 484
New Glasgow, Nova Scotia
B2H 5E5
(902) 755-1785

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

FMC Chemicals
570-875 Dunsmuir Street
Vancouver, British Columbia
V6C 1N5
(604) 685-6508

Great Lakes Forest Products
Duke Street
Dryden, Ontario
P8N 2Z9
(807) 223-2323

Prince Albert Pulp Company Ltd.
Saskatoon Chemicals Division
P.O. Box 1586
Saskatoon, Saskatchewan
S7K 3R3
(306) 652-9456

St. Anne Chemical Co.
8 Prince Arthur Avenue
Toronto, Ontario
M5R 1A9
(416) 968-2900

Stanchem
Division of PPG Industries Canada
Limited
5029 St. Ambroise Street
Montreal, Quebec
H4C 2E9
(514) 933-6721

3.3 Major Transportation Routes

Current Canadian production and use of chlorine is widespread. The largest production facilities are located in Fort Saskatchewan, Alberta; near Quebec City and Montreal, Quebec; in Sarnia, Ontario; and in Vancouver, B.C.

3.4 Production Levels (Corpus 1983)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1982)
CIL, Becancour, Que.		295
CIL, Cornwall, Ont.		37
CIL, Dalhousie, N.B.		28
Canadian Occidental, Vancouver, B.C.		141
Canadian Occidental, Harmac, B.C.		28
Dow Chemical Canada, Sarnia, Ont.		318
Dow Chemical Canada, Ft. Saskatchewan, Alta.		476
FMC Chemicals, Sqamish, B.C.		68
Great Lakes Forest Products, Dryden, Ont.		14.5
Prince Albert Pulp, Saskatoon, Sask.		33
St. Anne Chemical, Nackawic, N.B.		33
Stanchem (PPG), Beauharnois, Que.		116
	TOTAL	1,587.5
Domestic Production (1982)		1,233.3
Imports (1982)		21.4
	TOTAL SUPPLY	1,254.7

3.5 The Manufacture of Chlorine (Shreve 1977)

3.5.1 General. Chlorine is produced in Canada through the electrolytic decomposition of brine.

3.5.2 Manufacturing Process. There are three types of electrolysis cells: the mercury, diaphragm, and membrane cells. The use of mercury cells has declined substantially due to the implementation of stringent government regulations controlling the use of mercury. Only the diaphragm and membrane cells will be discussed in this section.

The diaphragm cell employs a diaphragm to separate the two electrodes. In the operation of the cell, brine is fed into the anode section where chlorine is formed; sodium ions pass through the diaphragm to the cathode where sodium hydroxide is formed. This process is represented by the following equation:

$$NaCl(aq) + H_2O \rightarrow \underset{\text{(cathode)}}{NaOH(aq)} + \underset{\text{(cathode)}}{1/2\ H_2(g)} + \underset{\text{(anode)}}{1/2\ Cl_2(g)}$$

The use of diaphragms permits the construction of compact cells with lower resistance. In principle, the diaphragm permits the free flow of ions and discourages the diffusing of electrolysis products. In fact, the sodium chloride solution can migrate through the pores in the diaphragm and the caustic can back migrate through the diaphragm to the anode. The former produces caustic with substantial amounts of sodium chloride; the latter migration produces oxygen which dilutes the chlorine produced and attacks the anode.

To overcome the disadvantages of the diaphragm cell, new ion-selective membranes have been developed to separate the anode and cathode. These new membranes permit the production of higher-strength caustic and reduce the need for investment in downstream cleanup processes. The membranes are typically fluorocarbons. Some developers are improving the design and efficiency of the new cells by actually bonding the electrodes directly to the membrane. Another developer is working on a new cell that uses the energy of the byproduct (hydrogen) to purify and concentrate the sodium hydroxide by electrodialysis and to concurrently generate part of the electricity required for operation of the cell. The cell is all plastic and uses porous, catalyzed electrodes, very narrow gaps, and a special cation exchange dialysis membrane. Because the cell is free of chlorine it can use low-cost hydrocarbon-based membranes (Chemical Week, 1981).

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

Chlorine is used in the pulp and paper industry, in mining and smelting industries, and for water treatment. It is used in the production of aluminum chloride, phosgene, sodium hypochlorite, ethylene dichloride, chlorinated solvents, propylene oxide, chlorinated phenols, chloracetic acid, carbon tetrachloride, and hydrogen chloride.

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

Abitibi-Price, Smooth Rock Falls, Ont.
American Can, Marathon, Ont.
B.C. Forest Products, Crofton, B.C.
Bartek Chemical, Burlington, Ont.
Bayer Canada, Mississauga, Ont.
Boise Cascade, Ft. Frances, Ont.; Newcastle, N.B.
Bristol-Myers, Toronto, Ont.
Canadian Cellulose, Prince Rupert, B.C.
Canadian Forest Products, Port Mellon, B.C.
Canadian Int'l Paper, La Tuque, Que.; Hawkesbury, Ont.
Canadian Liquid Air, Montreal, Que.
Canadian Miraclean, Vancouver, B.C.
Capo Polishes, Burlington, Ont.
Cariboo Pulp, Quesnel, B.C.
Chlorox, Bramalea, Ont.
Cornwall Chemicals, Cornwall, Ont.
Crestbrook Forest Ind., Skookumchuk, B.C.
Crown Zellerback, Campbell River, B.C.
Diversey Wyandotte, Mississauga, Ont.
Domtar, Cornwall, Ont.
Eddy Forest Products, Espanola, Ont.
Ethyl Canada, Sarnia, Ont.
Finnan Engineered Products, Montreal, Que.
Fraser Atholville, Edmundston, N.B.
Great Lakes Forest Products, Thunder Bay, Ont.
Harrisons & Crosfield, Toronto, Ont.
Inco, Thompson, Man.
Intercontinental, Prince George, B.C.
International Chemical, Brampton, Ont.
Irving Pulp, Saint John, N.B.
Kimberly-Clark, Terrace Bay, Ont.
Lavo, Montreal, Que.
MacMillan Bloedel, Harmac, B.C.
Matheson of Canada, Brampton, Ont.
Montreal Municipality, Que.
Northwood Pulp, Prince George, B.C.
Nova Scotia Forest Industries, Pt. Tupper, N.S.
Prince George Pulp, Prince George, B.C.
Rayonier Canada, Port Alice, Squamish, B.C.
St. Anne-Nackawic, Nackawic, N.B.
St. Regis (Alberta), Hinton, Alta.
Scott Maritimes, Abercrombie Pt., N.S.
Tahsis, Gold River, B.C.
Thurso Pulp & Paper, Thurso, Que.
Toronto Metro, Ont.
Uniroyal, Ft. Saskatchewan, Alta.
Weyerhaeuser, Kamloops, B.C.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 General. Liquid chlorine is usually transported in steel containers and vessels equipped with safety devices and pressure tested at regular intervals.

The three basic containers approved by the Chlorine Institute are cylinders, ton containers, and single-unit railway tank cars (CM 1970). Special railway tank cars called TMU or multi-unit tank cars, built to carry 15 of the above-mentioned ton containers, and tank motor vehicles, though seldom in use to transport chlorine in Canada, are also included in this report.

4.1.2 Cylinders. Chlorine cylinders are of seamless steel construction with a capacity of 0.45 to 68.2 kg (1 to 150 lb.); those of 45.5 and 68.2 kg capacity predominate (Dow CH 1966). Cylinders of 68.2 kg capacity have tare weight ranges of 54.5 to 63.6 kg (heavy) and 38.6 to 47.7 kg (light); outside diameters of 266.7 to 273 mm (10.5-10.8 in.) (heavy) and 260 to 237 mm (light); and lengths of 1,346 to 1,422 mm. Cylinders must comply with CTC/DOT specifications 3A480, 3AA480, 25, 3, 3BN480, 3E1800 and B.E.25. Class 3A and 3AA cylinders having higher service pressures also may be used. Each specification is described in Table 2 (CM 1976). Common cylinders are illustrated in Figure 7.

The Chlorine Institute has designed a standard cylinder valve equipped with a fusible metal type safety relief device designed to melt at temperatures between 70°C and 73.9°C (CM 1976).

4.1.3 Ton Containers. The chlorine ton container is a welded steel tank carrying a net mass of up to 1,091 kg (2,405 lb.). It must comply with CTC/DOT specifications 106A500, 106A500X, ICC27 and B.E., each described in Table 3. The ton container is 2,026-2,096 mm (79.8-82.5 in.) in length and 762 mm (300 in.) in diameter (CM 1976). The heads are concave. The sides are crimped inward to each end to form chimes which facilitate lifting. A few containers have compound curvature on the head opposite the valves (CM 1976).

The container is equipped with two identical valves near the centre of one end. The Chlorine Institute has designed a standard ton container valve which differs from the standard cylinder valve only in that it has no fusible metal plug and has a larger internal passage. Each valve connects to an internal eduction pipe. The valves are protected by a removable steel valve protection hood (CM 1976).

TABLE 2 CYLINDER SPECIFICATIONS

CTC/DOT* Specification Number	Description
3A	Seamless steel cylinder. Maximum service pressure 1,035 kPa.
3A480	Same as 3A except maximum service pressure 3,312 kPa.
3AA	Seamless steel cylinder. Maximum service pressure 1,035 kPa. Steels definitely prescribed. Maximum carbon content 0.28%.
3AA480	Same as 3AA except maximum service pressure 3,312 kPa.
3BN480	Seamless nickel cylinder. Maximum service pressure 3,312 kPa.
3E1800	Seamless steel cylinder. Maximum service pressure 12,400 kPa. Maximum diameter 50 mm. Maximum length 610 mm.

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

TABLE 3 TON CONTAINER SPECIFICATIONS

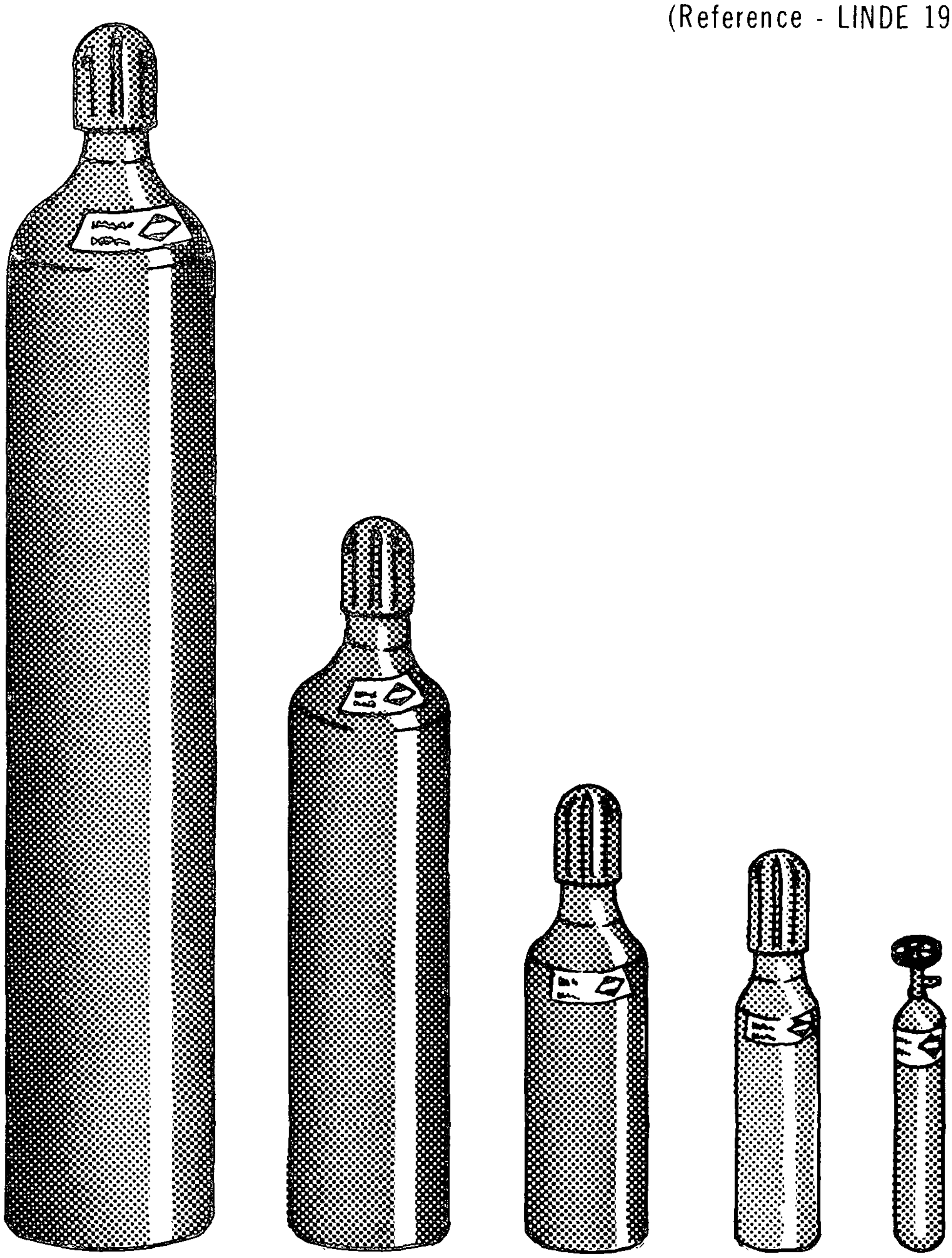
CTC/DOT* Specification Number	Description
106A500	Steel forge welded tank. Test pressure 3,450 kPa.
106A500X	Steel tank. Fusion welded longitudinal tank seam. Forge welded head seam. Test pressure 3,450 kPa.
1CC27	Steel forge welded tank. Test pressure 3,450 kPa.

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

FIGURE 7

COMMON GAS CYLINDERS

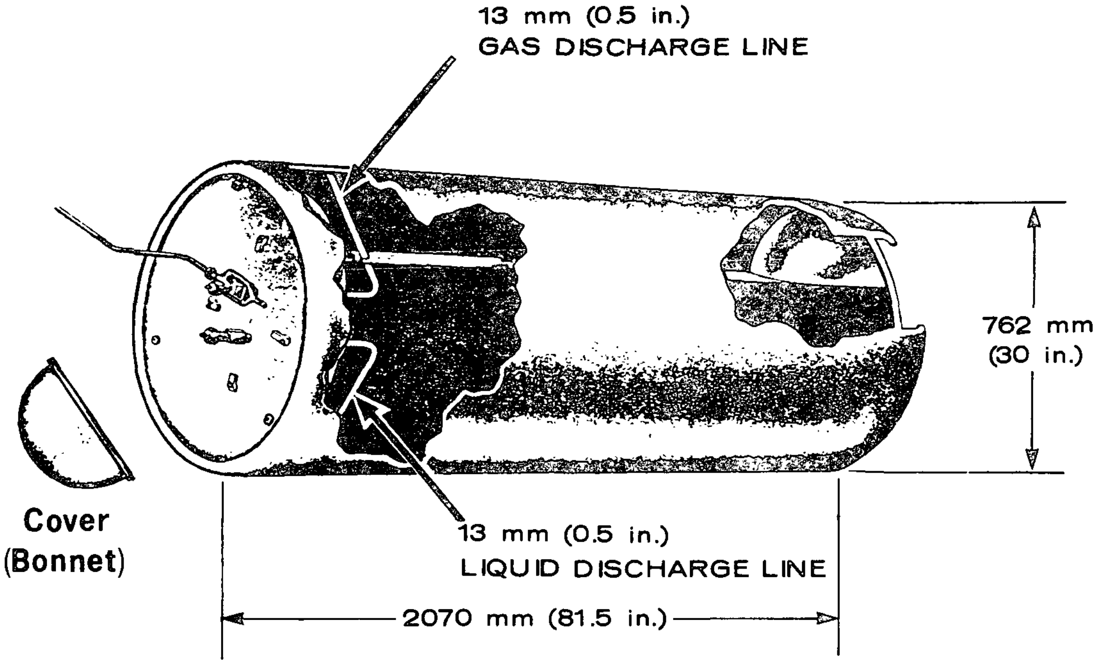
(Reference - LINDE 1981)



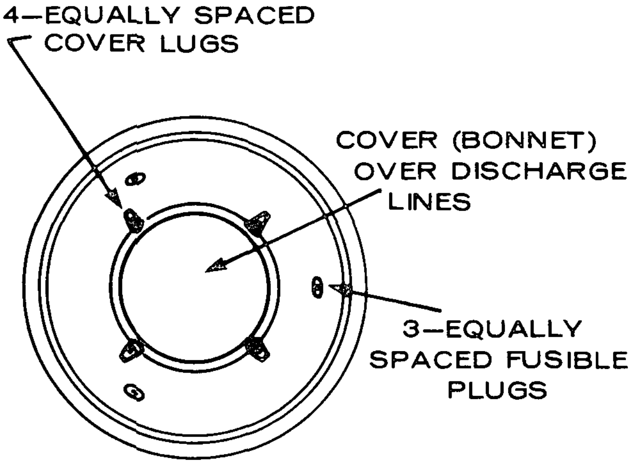
Industry designation		K	Q	G	F	LB
Approx. size	(mm)	229×1320	178×787	152×508	102×432	51×330
	(in)	9×52	7×31	6×20	4×17	2×13
Approx. weight (empty)	(kg)	60	29	13	5	2
	(lb)	132	65	29	10	4

CHLORINE TON CONTAINER

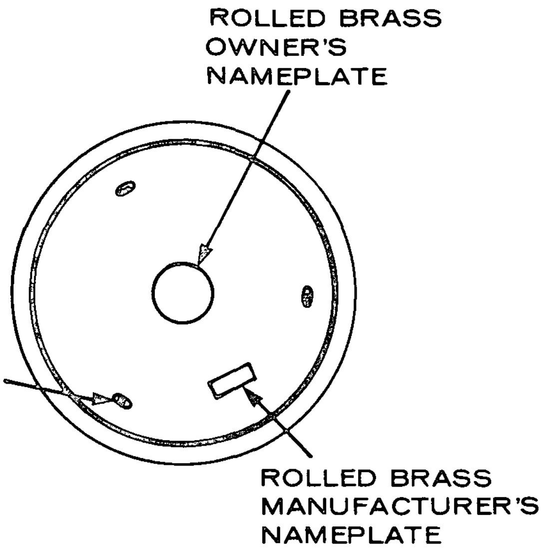
(Reference – CM 1976)



Cutaway view of side



View of loading end



View of blank end

All containers are equipped with fusible metal type safety relief devices. Most have six fusible metal plugs, three in each end, spaced 120° apart. The fusible metal is designed to melt between 70°C and 73.9°C (CM 1976).

4.1.4 Railway Tank Cars. Constructed of steel, railway tank cars are most typically designed to transport a chlorine net mass of 55 or 90 tonnes (TCM 1979; ORER 1983). Cars must comply with CTC/DOT specifications 105A500 or 105A500W, described in Table 4. Tank cars require cork insulation or other suitable material protected by a steel jacket (TCM 1979). A typical railway tank car is illustrated in Figure 9; Table 5 indicates railway tank car details associated with this drawing. The only opening permitted in the tank is a single manway located in the centre at the top. Five valves are mounted inside the dome cover as shown schematically in Figure 10. Four of these are angle valves; the fifth, mounted in the centre, is a safety relief valve.

TABLE 4 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
105A500	Steel forge-welded tank with manway. Insulated. Top unloading arrangement required. Safety valve set at 2,590 kPa (375 psi). Bottom outlet or washout prohibited.
105A500W	Same as 105A500 but fusion-welded.

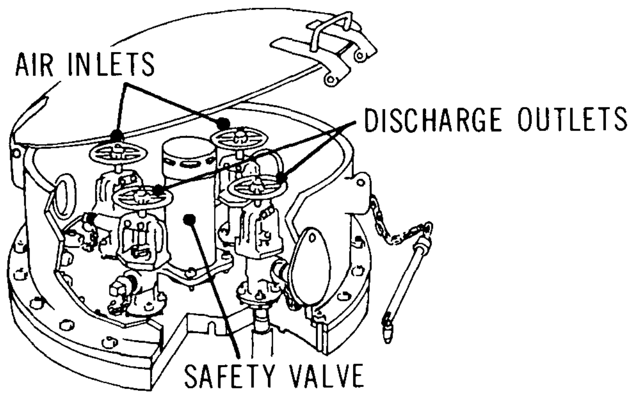
*Canadian Transport Commission and Department of Transportation (U.S.)

The Chlorine Institute has designed a standard angle valve. Two angle valves on the longitudinal centre line of the car are for unloading liquid chlorine. The two angle valves on the transverse centre line are connected to the vapour space.

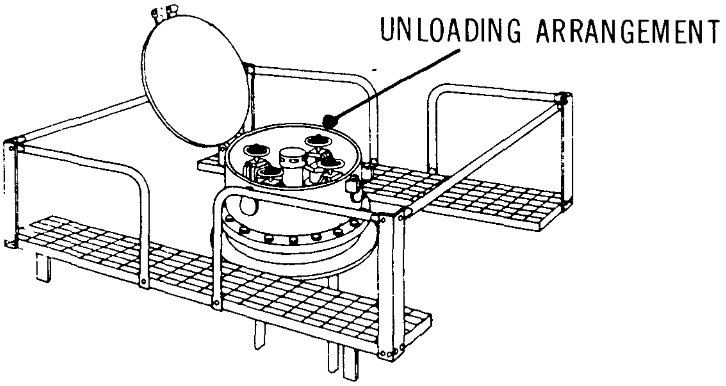
Under each liquid valve is an eduction pipe fastened to the manway cover and extending to the bottom of the tank. At the top of each eduction pipe, immediately below the manway cover, is a rising-ball, excess-flow valve designed to close when the rate of flow of liquid chlorine exceeds about 6,800 kg/h. This is a protective device designed to automatically stop the flow of liquid chlorine if the angle valve is broken off or, under certain conditions, if the unloading line is severed (CM 1970). The safety relief valve is of the spring-loaded type and is usually combined with a breaking pin assembly.

RAILWAY TANK CAR - CLASS 105A500W

(Reference - TCM 1979; RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

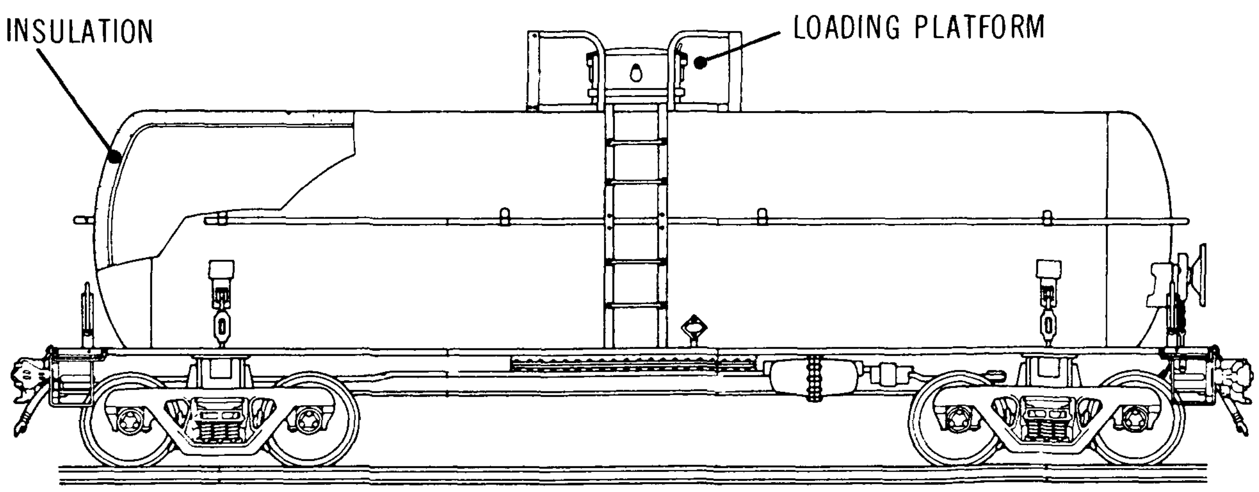


Illustration of tank car layout

TABLE 5 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A500W (TCM 1979; RTDGR 1974)

	Tank Car Size (Imp. gal.)	
Description	8,800	15,000
Overall		
Nominal capacity	40,000 L (8,800 gal.)	68,000 L (15,000 gal.)
Car weight- empty	33,800 kg (74,600 lb.)	37,400 kg (82,500 lb.)
Car weight- (max.)	99,800 kg (220,000 lb.)	106,400 kg (263,000 lb.)
Tank		
Material	Steel	Steel
Thickness	17-24 mm (11/16-15/16 in.)	17-24 mm (11/16-15/16 in.)
Inside diameter	2.2 m (88 in.)	2.6 m (102 in.)
Test pressure	3,450 kPa (500 psi)	3,450 kPa (500 psi)
Burst pressure	8,620 kPa (1,250 psi)	8,620 kPa (1,250 psi)
Approximate Dimensions		
Coupled length	13 m (41 ft.)	15 m (48 ft.)
Length over strikers	12 m (39 ft.)	14 m (46 ft.)
Length of truck centres	9 m (28 ft.)	11 m (35 ft.)
Height to top of grating	4 m (12 ft.)	4 m (12 ft.)
Overall height	5 m (15 ft.)	5 m (15 ft.)
Overall width	3.2 m (127 in.)	3.2 m (127 in.)
Length of grating	2-3 m (7-10 ft.)	2-3 m (7-10 ft.)
Width of grating	1.5-2 m (5-6 ft.)	1.5-2 m (5-6 ft.)
Loading/Unloading Fixtures		
Unloading Connection	25 mm (1 in.) via valve and 32 mm (1 1/4 in.) check valve	
Valving	2 unloading connections and 2 valves to vapour space	
Safety Devices	Safety relief valve set at 2,590 kPa (375 psi)	
Insulation	102 mm (4 in.) foam or cork insulation	

4.1.5 Multi-unit Railway Tank Cars. A multi-unit tank car used in chlorine transportation consists of an under-frame on which 15 ton-containers are mounted (CM 1970). Cranes or other lifting devices of at least 2,000 kg capacity should be used when loading or off-loading ton containers. Also, a proper lifting beam should be utilized (CM 1970).

4.1.6 Tank Motor Vehicles. Chlorine tank motor vehicles consist of a cargo tank pulled by a tractor. The maximum tank capacity is restricted by highway load limits.

FIGURE 10

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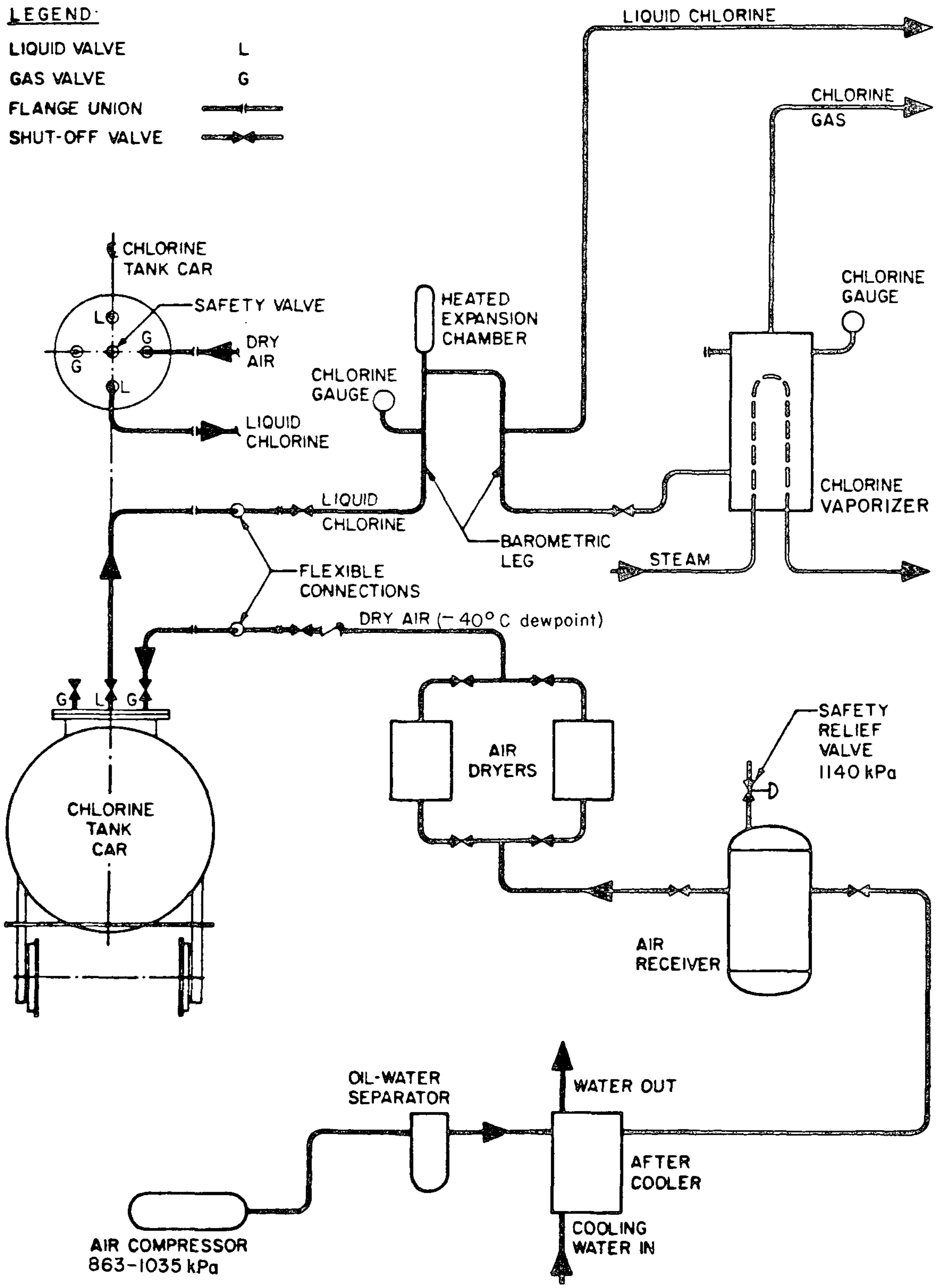
TANK CAR UNLOADING



They must comply with TC/DOT specifications MC331 or TC331 as outlined in Table 6. Most tanks have a chlorine capacity of 14 to 18 tonnes but range as high as 29 tonnes (HCG 1981).

TABLE 6 TANK MOTOR VEHICLE SPECIFICATIONS

TC/DOT* Specification Number	Description
MC331 (or TC331)	Seamless or welded steel tank. Design and construct in accordance with ASME code. One opening with protective housing and manway cover. Maximum design pressure 3,450 kPa (500 psi). Insulated. Postweld heat treatment as per ASME code. Gauging device prohibited.

*Transport Canada and Department of Transportation (U.S.)

All tanks are provided with 100 mm of insulation protected by a steel jacket. The only tank opening permitted is a manway located at the top. The valve arrangement is the same as that on tank cars except that excess-flow valves are also required under the gas valves. The operating angle valves are the same as those on tank cars (CM 1970). Immediately below each liquid angle valve there is an excess-flow valve and an eduction pipe the same as those on tank cars. In addition, under each gas valve there is an excess-flow valve of different design, used to prevent outward flow of gas if the angle valve is broken off (CM 1970).

The safety relief valve is of the spring-loaded type and always is combined with a breaking pin assembly. On all tanks, the pin is designed to function at 1,550 kPa (225 psi).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Cylinders and Ton Containers. Both cylinders and ton containers are handled and stored in the same manner. The following points should be observed when handling and storing containers (CM 1970):

- Valve protection hoods should be in place.
- Containers should not be stored near ventilating systems.

- Store to minimize external corrosion.
- Store cylinders upright, ton containers on their sides.
- Store full and empty containers separately.

Cylinders deliver chlorine gas when in an upright position and liquid when in an inverted position. Ton containers, when in a horizontal position and with the valves in a vertical line, deliver gas from the upper and liquid from the lower valve (CM 1970).

A flexible copper connection capable of withstanding a pressure of 3,450 kPa (500 psi) should be installed between the container and the piping system (Dow CH 1966).

Yokes and adapters are recommended for connection to the container valve outlet (CM 1970). A barometric leg, similar to that shown in Figure 8, or a vacuum-breaking device should be used when using chlorine cylinders or ton containers. It should be remembered that when chlorine is being fed into a liquid, the liquid can be sucked back into the container (CM 1970).

4.2.2 Off-loading Equipment and Procedures for Railway Tank Cars and Tank Motor Vehicles. Chlorine railway tank cars and tank motor vehicles are basically off-loaded in the same manner but only after the following precautionary steps have been undertaken (CM 1970):

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

The chlorine railway tank car or highway vehicle may be unloaded by vapour pressure or by air padding. When using the vapour pressure method, chlorine liquid is discharged from one of the two liquid angle valves. When chlorine gas is required, the liquid chlorine should be vaporized; chlorine gas should not be discharged from gas angle valves (CM 1970). During the air padding method, dry air is used to increase car pressure as schematically indicated in Figure 10 (CAP 1961).

After unloading lines have been disconnected, valve outlet plugs should be immediately replaced to prevent thread corrosion by atmospheric pressure.

4.2.3 Specifications and Materials for Off-loading Equipment. In this section, the components of a typical off-loading system handling dry chlorine at commonly employed temperatures and pressures will be discussed. These include piping, flexible connections, flanges and fittings, valves, gaskets, gauges, rotameters, vaporizers, expansion chambers and air padding equipment.

Piping should be of Schedule 80 seamless or carbon steel (Dow CH 1966). Cast iron piping, fittings or equipment should never be used for chlorine service, since the possibility of failure is greater with such materials and the consequences of failure are likely to be serious. All pipe purchased ready-bent should be specified as bent hot (Dow CH 1966).

Pipeline joints should preferably be flanged or welded. If threaded joints are necessary, extreme care must be taken to obtain clean, sharp pipe threads, in order to ensure pressure-tight joints. A small amount of a linseed oil and white lead paste may be used as a pipe dope. The dope should be applied to the male thread only in such a manner as to prevent its entrance into the piping system. Teflon tape or paste may be used as a pipe sealant provided caution is used during installation to prevent fragments from entering the piping system (CE 1981). For permanent joints, freshly prepared litharge and glycerine are also satisfactory (Dow CH 1966).

Flexible connectors, consisting of a flexible Monel hose or a loop of copper or copper alloy, should be installed between containers and rigid piping systems (LC). Seamless copper water tubing per ASTM B88 in the annealed state with Type K wall thickness, or heavier, is recommended. Connectors for chlorine railway tank cars and motor vehicles should terminate in 25 mm 300-ANSI B16.5 forged steel flanges (CM 1970).

Forged-steel 300-pound weld neck flanges, slip-on welding flanges, or threaded flanges, all with ASA small tongue-and-groove facings, faced and drilled, are acceptable, as are forged-steel tongue-and-groove ammonia flanges (Dow CH 1966).

Acceptable fittings include Schedule 80 forged-steel welding tees and elbows, cast steel 300-pound flanged elbows, and tees with ASA faced and drilled small tongue-and-groove facings, and forged-steel 2,000-pound screw-end elbows and tees (Dow CH 1966).

Specially designed indicating O.S. and Y or rising stem valves having black iron, drop-forged carbon steel, or bronze bodies, and stems and trim of Monel metal or Hastelloy C nickel alloy are recommended for chlorine service. Glands should be bolted rather than screwed, since the threads of the latter may be quickly attacked by wet chlorine vapour. Non-armored porcelain valves should be avoided because of the likelihood of failure in service (Dow CH 1966). Asbestos impregnated with Teflon, graphite-lubricated asbestos, and rubberized cotton cordage lubricated with beeswax or graphite are common packing materials (Dow CH 1966).

Valves should be dismantled and cleaned of oil before use. Before installation, valves should be tested for seat tightness at 1,035 kPa (150 psi) with dry air having a dew point of -40°C or below (Dow CH 1966).

Gaskets should be of 3 percent antimony lead or of bonded asbestos fiber as per Military Specification MIL-A-17472 (Navy) or equivalent. For pipe smaller than 50 mm, 1.6 mm thick gaskets should be used; for pipe 50 mm or larger, gaskets should be 3 mm thick. Rubber gaskets are attacked by liquid chlorine and should never be used (Dow CH 1966).

Pressure gauges should be designed for chlorine service and be either the diaphragm-protected type or the forged-steel welded bourdon tube type. Diaphragms may be made of Monel, silver or tantalum. A pressure range of not less than 1,725 kPa (250 psi) is desirable (Dow CH 1966).

The flow of liquid and gaseous chlorine can best be determined by rotameters which are specially designed for chlorine service (LC). Where a rotameter is used in the gas phase, regular maintenance of the instrument is required if accurate measurements are to be obtained. Any orifice installation on gas service should conform to good engineering practice, as outlined in literature such as the "Flow Meter Engineering Handbook" published by Honeywell, or the American Gas Association Measurement Committee Report No. 3, "Orifice Metering of Natural Gas" (CE 1981).

Chlorine is converted from the liquid to the gaseous state by use of a vaporizer - a device consisting essentially of an evaporating manifold constructed of carbon steel pipe surrounded by a jacket through which hot water or steam is passed. (With steam, the temperature should be less than 130°C.) The liquid chlorine enters the manifold and vaporizes instantly. The chlorine gas is vented through the top of the evaporator (Dow CH 1966).

Liquid chlorine lines should be protected with expansion chambers of at least 20 percent of pipe volume between shut-off valves. An inverted cylinder located at the highest point in the pipe line will serve this purpose. A typical expansion chamber consists of a rupture disc, pressure indicator, chamber and appropriate fittings. In the event of the line valves being closed and the temperature of the liquid chlorine rising, the expansion chamber will absorb the resultant increase in volume of the trapped liquid chlorine and thereby eliminate the possibility of hydrostatic rupture of the line. Where an expansion chamber is to be located outdoors, it should be steam traced (CM 1970). Liquid chlorine lines may also be protected by using safety release valves (CCPA 1982).

Air padding is somewhat hazardous unless suitable equipment is used and approved procedures are followed. An approved air-padding unit consists of a suitable air compressor, an ASME Code receiver, an after-cooler, a water and oil separator, and an air drier, as previously illustrated in Figure 10 (CAP 1961). The compressor should be of standard design with an automatic pressure control and should be separate from the plant air system. A variety of driers may be used provided they are capable of drying the air to a dew point of -40°C measured at the tank car pressure. The air receiver must be equipped with a pressure gauge, a safety valve, a drain valve and automatic pressure controls (CAP 1961).

4.3 Emergency Off-loading Equipment and Procedures

Emergency railway tank cars and tank motor vehicles would be similar to those previously described in this report. These would receive liquid chlorine transferred from damaged or leaking railway or highway tankers. In addition, emergency shut-off facilities may be installed at the chlorine tank car loading and unloading stations (ESF 1965). This would prevent a major leak from occurring if, for example, a switch engine moved a tank car that was loading or unloading chlorine, thereby rupturing the connection. Such a system would consist of a pneumatically actuated control valve with a pressure switch downstream. The reduced pressure caused by a major leak would open the pressure switch contacts and by use of a solenoid valve, vent the air normally supplied to the control valve, thereby causing it to close and stop chlorine leakage (ESF 1965).

4.4 Compatibility with Materials of Construction

The compatibility of chlorine with materials of construction is indicated in Table 7. The unbracketed abbreviations are described in Table 8. 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 7 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

	Chemical		Material of Construction		
Application	State/ Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings			Schedule 80 Seamless Steel 300 lb. Malleable iron or 200 lb. Forged Steel Fittings (HOC 1972)		PVC (HOC 1972) or CI Malleable Fittings (PAE 1968)
			Welded Black Iron or Steel with Ammonia flanges; Gaskets of Asbestos or 3% Antimony Lead		Cold Bent CS (PAE 1968)
			Copper (LC)		
	Dry Gas	23		ABS PVC I PVC II (DPPED 1967)	PE (DPPED 1967)
	Dry Gas	60		PVC I (DPPED 1967)	PVC II (DPPED 1967)
	Dry Gas	71			ABS (DPPED 1967)
	Dry Gas				PVC I* ABS* PE (MWPP 1978)
	Dry Gas	93	PVDF (DCRG 1978)		
	Dry Gas	24	Chlorinated Polyether PP PVDC (DCRG 1978)		

TABLE 7 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (continued)

	Chemical		Material of Construction		
Application	State/ Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (cont'd)	Wet Gas	23			PE ABS PVC I PVC II (DPPED 1967)
	Wet Gas	93	PVDF (DCRG 1978)		
	Wet Gas	24	Chlorinated Polyether PP PVDC (DCRG 1978)		
	Liquid	93	PVDF (DCRG) 1978)		
	Liquid				Chlorinated Polyether PP PVDC (DCRG 1978)
2. Valves			Bronze Body, Monel Stem and Seat; Carbon Steel Body, Teflon Seat, Monel Ball (HOC 1972)		Non-armored Porcelain Valves (PAE 1968)
	Dry Gas	21	SS 316 (JSSV 1979)		
	Wet Gas (Up to 2% Moisture)	21	SSJ-20 (JSSV 1979)	SS 316 (JSSV 1979)	

TABLE 7 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (continued)

	Chemical		Material of Construction		
Application	State/ Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
3. Storage	Liquid	20	CS ASTM A-612 - 72a GR.B CS ASTM A-516 - 72 GR.65 or 70		
4. Others				IIR EPDM (GPP)	NR SBR CR NBR CSM (GPP)
	Liquid	20	IIR EPDM CR FPM CSM (GF)		uPVC PE PP POM NR NBR (GF)
	Dry Gas 100%	20	uPVC FPM (GF)	PE PP CSM (GF)	POM NR NBR IIR EPDM CR (GF)
	Dry Gas	20		SS 302 SS 304 SS 316 (ASS)	SS 410 SS 430 (ASS)
	Wet Gas	20		SS 316 (ASS)	SS 302 SS 304 SS 410 SS 430 (ASS)
		100			SS 302 SS 304 SS 316 SS 410 SS 430 (ASS)

TABLE 7 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (continued)

	Chemical		Material of Construction		
Application	State/ Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
4. Others (cont'd)	Gas Dry or Wet	22			PVC (TPS 1978)
	Gas Dry or Wet	23			PP (TPS 1978)
	Gas Dry or Wet	66	PVDF (TPS 1978)		PP (TPS 1978)
	Liquid				PVC uPVC PP (TPS 1978)
	Gas, 90%	24-100	Glass (CDS 1967)		
	Gas, 100%	24-316	Glass (CDS 1967)		
	Gas, 90-100%	24	Wood-Cypress and Redwood (CDS 1967)		
	Liquid, 100%	24-100	Glass (CDS 1967)		

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

TABLE 8 MATERIALS OF CONSTRUCTION

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

5 CONTAMINANT TRANSPORT

5.1 General Summary

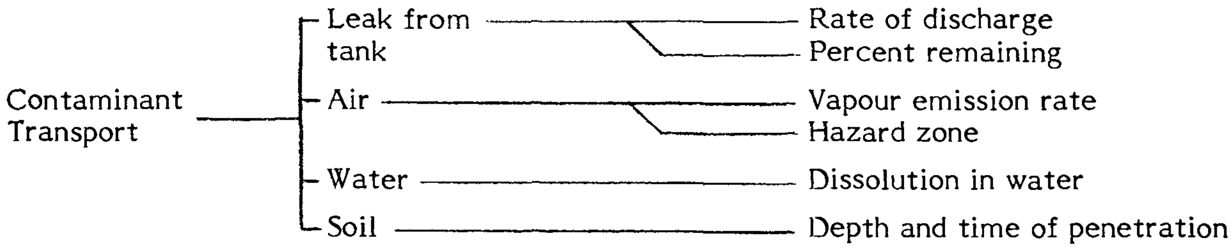
Chlorine is commonly transported in tank cars as a liquified compressed gas. It is generally released to the atmosphere in two ways: the continuous release of gas or liquid over a finite period of time, or an instantaneous release due to catastrophic failure of the container.

Examples of continuous release might include leaking cylinders or transfer piping, or puncture of a tank car where all of the contents have not been spilled. For this type of release, the liquid remaining in the container will cool to its boiling point (-34.6°C). A higher rate of release will cool it more quickly. Should the incident involve a tank car with a puncture hole of significant size, it is not uncommon for a crust of ice to form at the liquid chlorine surface. This phenomenon will reduce the rate of gaseous discharge or stop it. Any movement of the container or the contents can break this ice seal.

When liquid chlorine spills, part is immediately vaporized, cooling the remaining portion to its boiling point (-34.6°C). The result of a catastrophic spill, therefore, is an initial highly concentrated cloud of chlorine. This is followed by a slower, steady release of gas. The rate of this latter release depends on the rate of heat absorption from the surroundings. A pool of liquid chlorine at -34.6°C will vaporize at a slower rate on land than in water due to a poorer rate of heat exchange on land. The initial release due to catastrophic failure of a container is usually referred to as a flash off (puff). As an example, if a tank car containing 80,000 L of liquid chlorine at 25°C catastrophically ruptured and spilled its entire contents, about 25% (20,000 L) would flash off. The remaining liquid would spread on the ground forming pools in low places while continuously boiling off gas. If spilled on water, the remaining liquid chlorine would sink and boil. The vapour cloud, whether the spill occurred in water or on land, would tend to hug the surface and spread rather than lift off and disperse.

Chlorine spills on land may penetrate the surface depending on the soil type and its water content. Downward movement of the liquid to the groundwater may cause environmental problems.

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



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

5.2 Leak Nomograms

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

If a tank car loaded with chlorine is punctured on the bottom, all of the contents will be emitted. The instantaneous discharge rate (q) is a function of the height of the fluid above the hole (H), the internal pressure of the tank (P), the hole size (A) and shape, and a coefficient of discharge (C_d). For the purposes of nomogram preparation, the discharge coefficient has been assumed to be constant at 0.8.

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 has assumed to remain at a constant temperature, equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid has vaporized. The venting rate is a function of the internal tank pressure (P), which is the saturated vapour pressure (P_{sat}) of the liquid at temperature T. The assumed ambient temperature is 40°C, yielding a saturated vapour pressure (P_{sat}) of 1,200 kPa. The 40°C constant temperature assumption yields a high gas release rate from the tank and generally provides worst case values.

A worst case could be portrayed as a tank car that has been involved in an accident, has had most of its insulation damaged, has been punctured, and is in a fire. The fire would heat the damaged tank car and counteract the cooling of the liquid chlorine as it vaporizes. In this situation, all of the chlorine would be vented very quickly. However, in cold weather, with the insulation intact, the time period for all of the chlorine to escape from a punctured tank car would be several orders of magnitude greater (10^4-10^7). Thus, in a spill situation, it is important to determine the state of the insulation and the available external heat before estimating the amount of chlorine that is left in a tank car and the time it will take to empty.

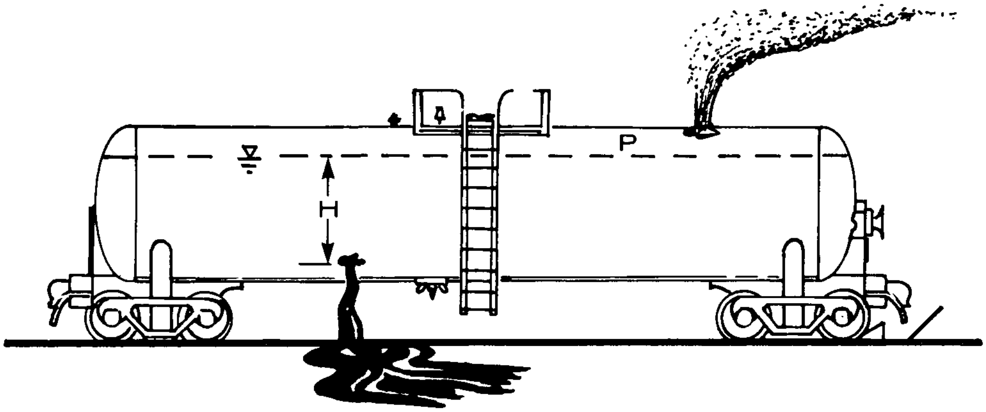


FIGURE 11 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

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

5.2.2 Nomograms.

5.2.2.1 Bottom puncture - liquid discharge.

Figure 12: Percent remaining versus time. Figure 12 provides a means of estimating the percent of chlorine remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car (2.75 m ∅ x 13.4 m long) is assumed to be initially full (at t=0) with a volume of about 80,000 L of chlorine at 40°C and 1,200 kPa. 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 13: Discharge rate versus puncture size. Figure 13 provides a means of estimating the maximum discharge rate (L/s), for a number of equivalent hole diameters. As the vapour 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 14: Percent remaining versus time. Figure 14 provides a means of estimating the percent of chlorine 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.

Figure 15: Venting rate versus puncture size. Figure 15 presents the relationship between venting rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For each hole size, the venting rate will be constant until all the liquid is vaporized. This is consistent with the assumption of constant temperature in the tank and results in a conservative estimate of the gas venting rate. The values presented in Figure 15 are independent of the tank car size, but assume that the liquid is at a constant temperature of 40°C and a saturated vapour pressure of 1,200 kPa.

5.2.3 Sample Calculations.

i) Problem A

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

Solution to Problem A

Step 1: Calculate amount remaining at t=1 min

- Use Figure 12
- With t=1 min and d=150 mm, the amount remaining is about 52 percent or 42,000 L

FIGURE 12

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PERCENT REMAINING vs TIME

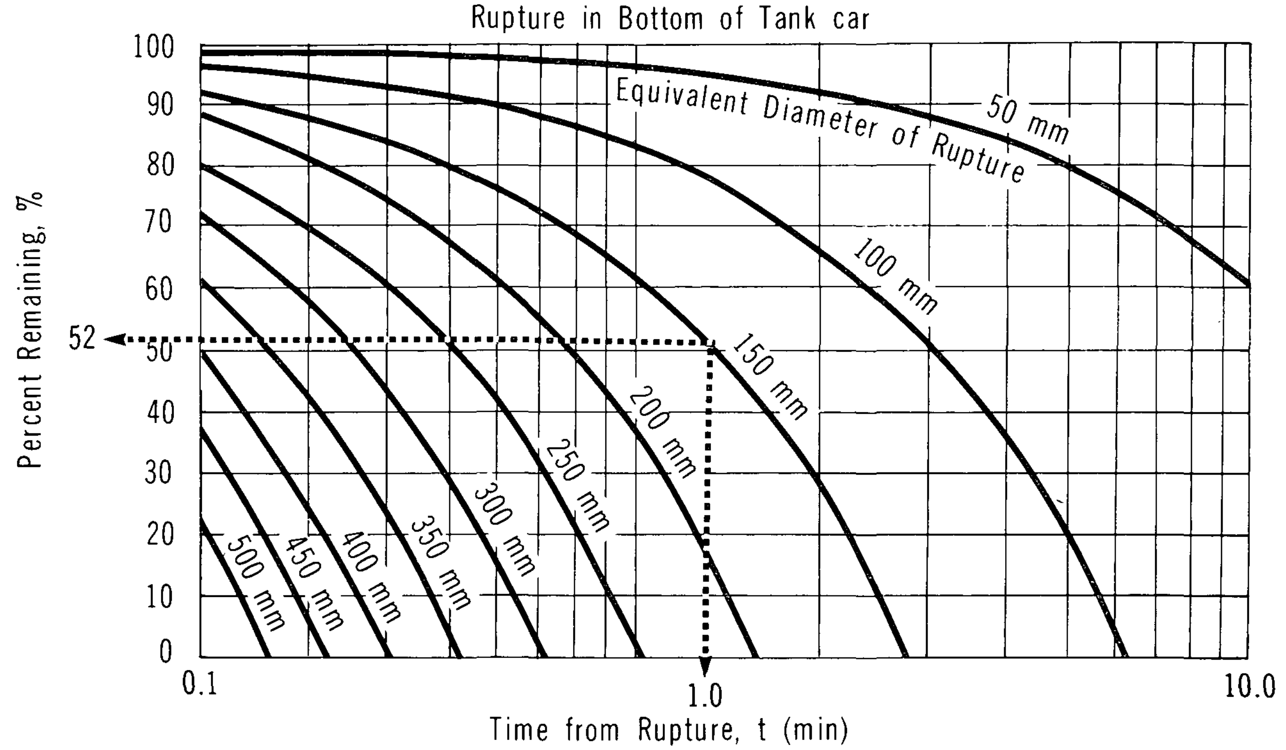

FIGURE 13

CHLORINE

DISCHARGE RATE vs RUPTURE SIZE

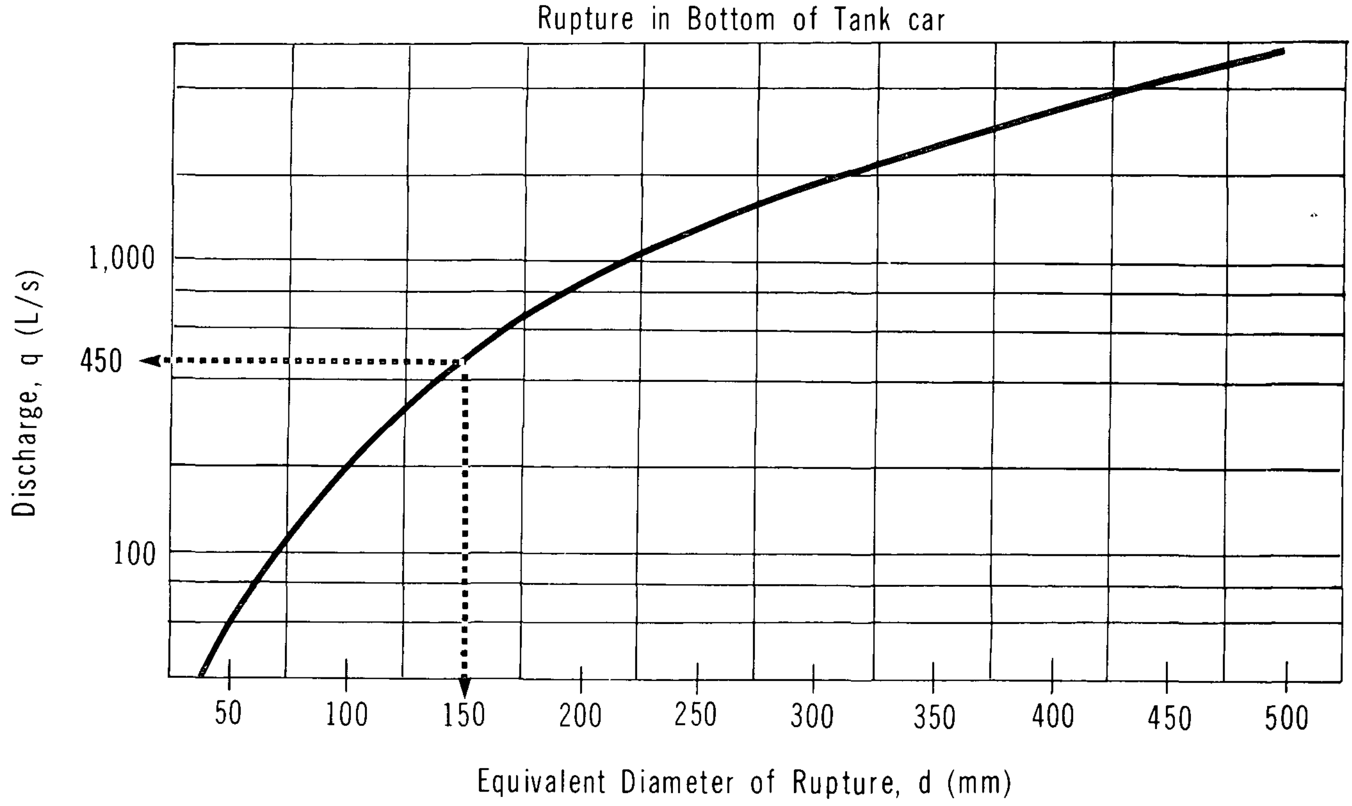

FIGURE 14

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PERCENT REMAINING vs TIME

Rupture in Top of Tank car

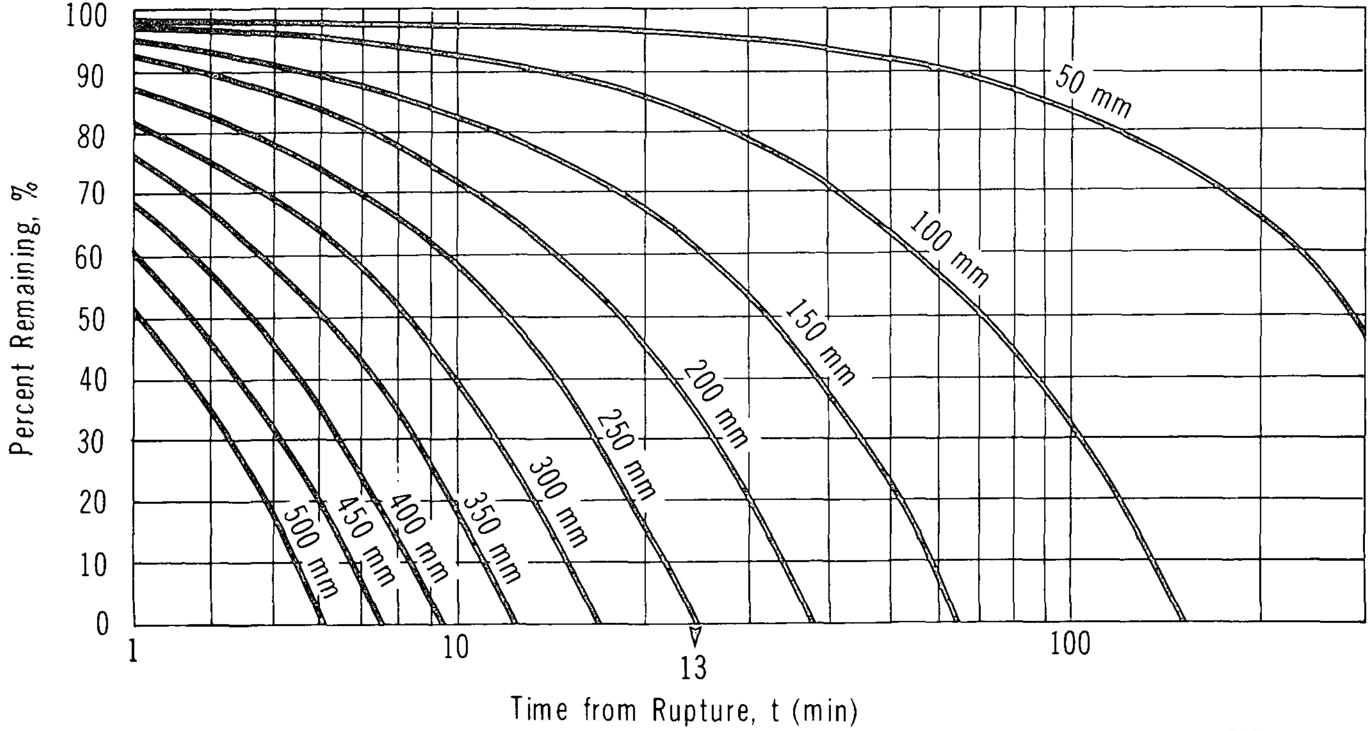
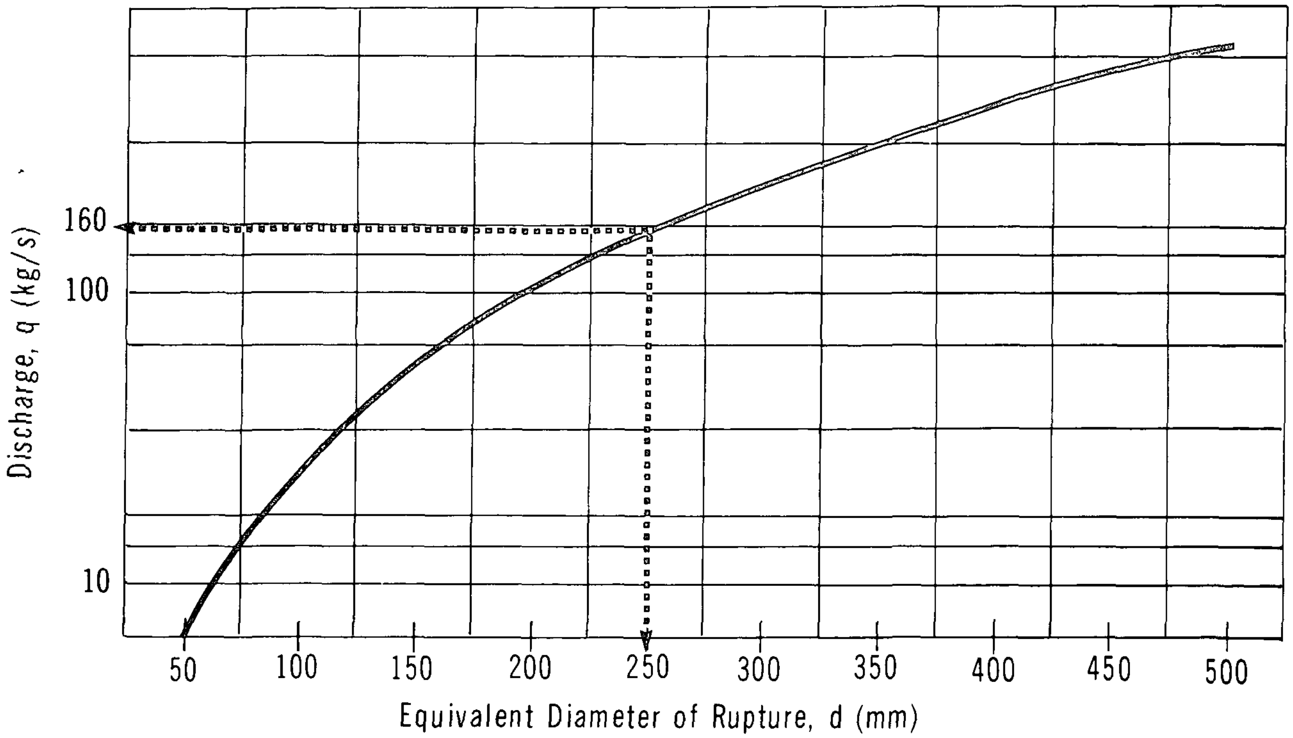


FIGURE 15

CHLORINE

DISCHARGE RATE vs RUPTURE SIZE

Rupture in Top of Tank car



Step 2: Calculate the discharge rate

- Use Figure 13
- With d=150 mm, the instantaneous discharge rate (q) = 450 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 a constant temperature of 40°C of the chlorine in the tank (worst case).*

Solution to Problem B

Step 1: Calculate the time to empty

- Use Figure 14
- With d=250 mm, the tank empties (0% remaining) in approximately 13 min

Step 2: Calculate the discharge rate

- Use Figure 15
- With d=250 mm and assuming chlorine is at a constant temperature of 40°C (worst case)*, the venting rate is constant at 160 kg/s

5.3 Dispersion in the Air

5.3.1 Introduction. Liquid chlorine under pressure is extremely volatile; thus, liquid chlorine spilled on ground or water in warm weather vaporizes rapidly enough to consider its vaporization as instantaneous, in the form of a puff. Only this chlorine release situation is treated here.

To estimate the vapour concentrations downwind of the accident site for the determination of the 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. Details of the model are contained in the Introduction Manual.

Figure 16 depicts schematically the contaminant plume configuration of a "puff" surface release. The dispersion model represents the spill as an instantaneous point source (with a total vapour release quantity, Q_T) equal to the amount of contaminant spilled.

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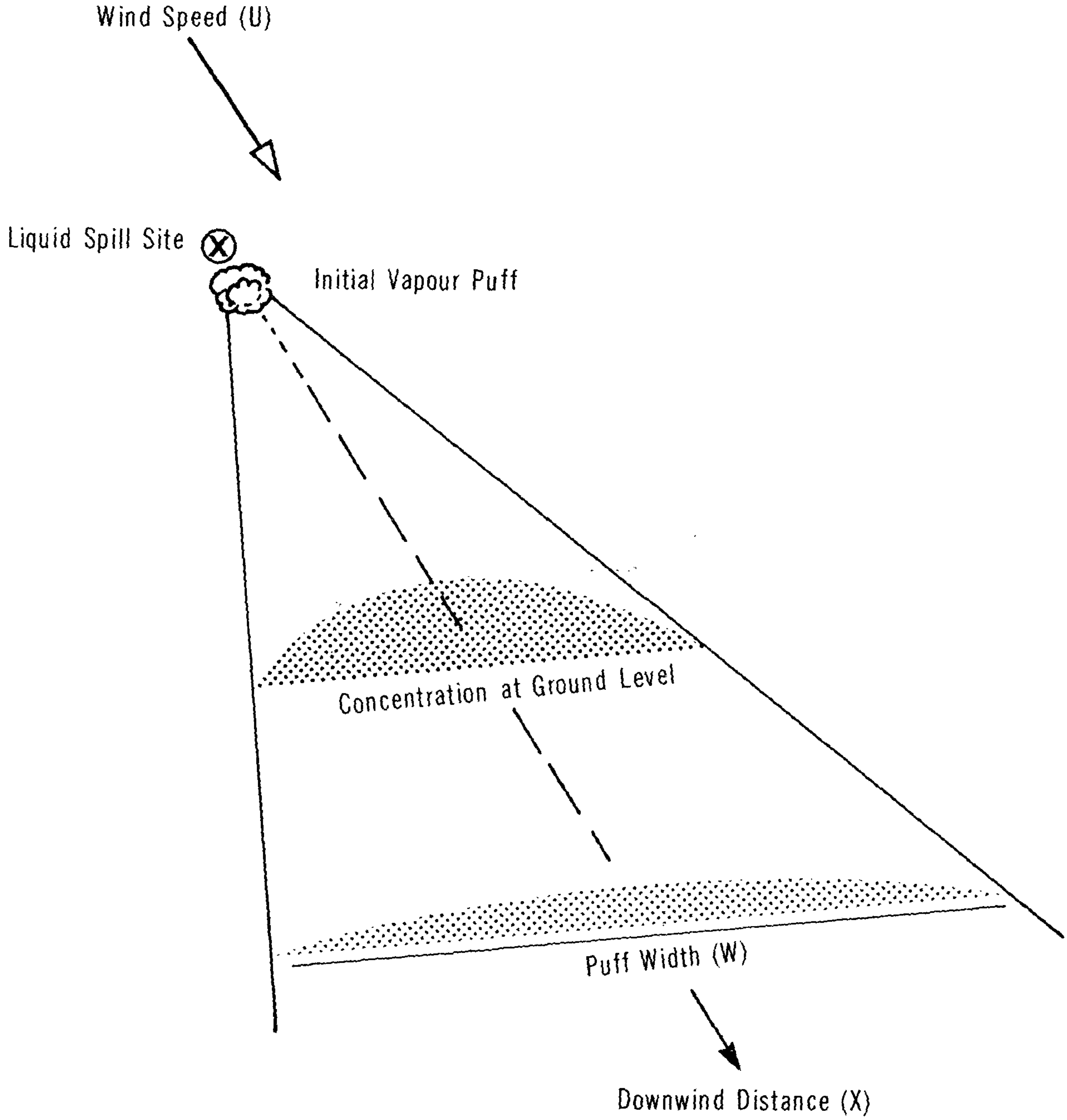
* Refer to section 5.2.1 for explanation of the assumptions.

SCHEMATIC OF CONTAMINANT PUFF



The use of the "puff" release model for spills of liquid chlorine will overestimate the hazard as a result of the spill, since only about 25 percent of the released liquid will instantaneously flash off as a puff (Howerton 1969). It should be noted that a chlorine vapour cloud rising from cold bulk liquid behaves as a heavier-than-air gas since the density of the vapour cloud is greater than that of air (2.4 times that of air at 20°C). Ground hugging and gas accumulation in low-lying areas may therefore be observed during the initial period. Conventional Gaussian modelling will tend to depict heavier-than-air plumes (puffs) to be narrower than observed.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud.

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

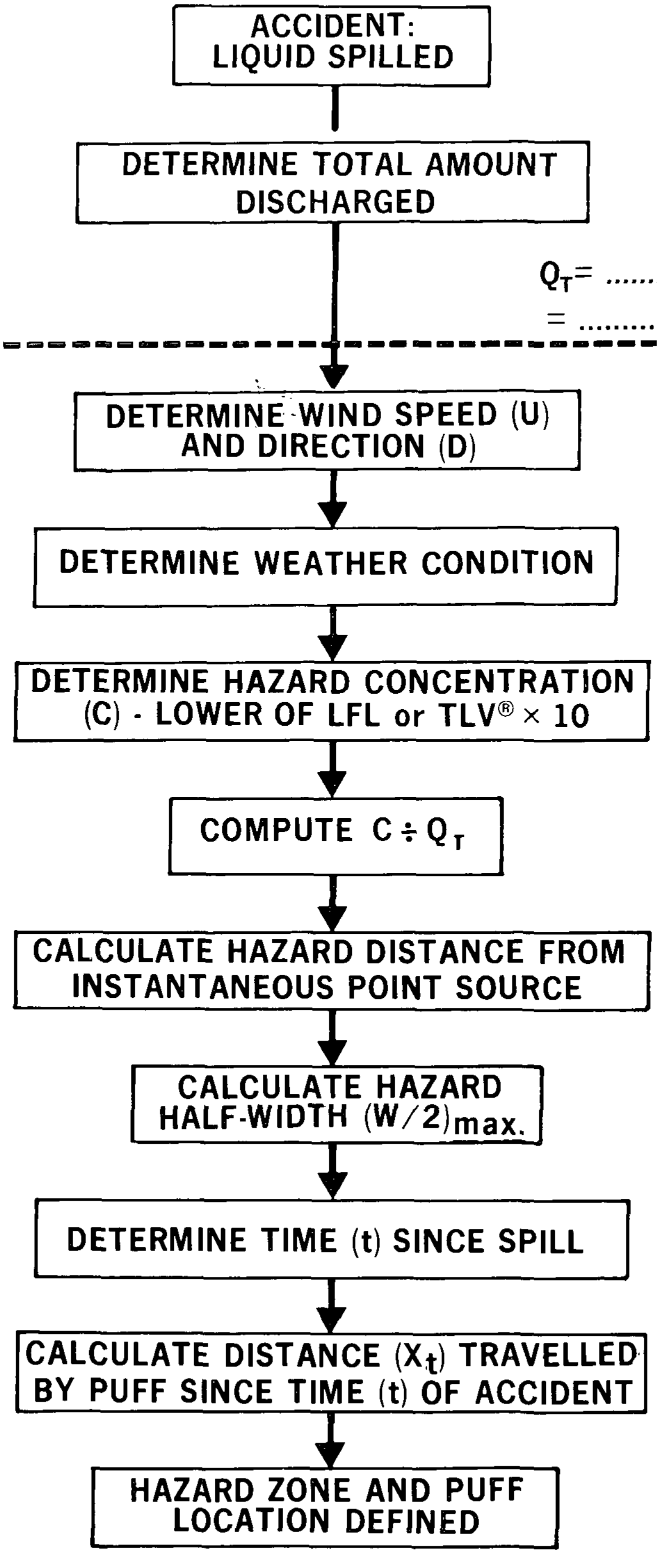
Table 9:	weather conditions
Figure 18:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 10:	maximum puff hazard half-widths
Figure 20:	vapour puff travel distance as a function of time elapsed since the spill and wind speed

The flow chart given in Figure 17 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" is contained in Section 5.2. A description of each vapour dispersion nomograms and its use follows.

5.3.2.1 Figure 18: Vapour concentration versus downwind distance. Figure 18 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 representated by the normalized, ground-level concentration (c/q_t, where c is the hazard concentration limit; see p. 43) at the centreline of the contaminant puff. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 18, the weather condition must be determined from Table 9.

FIGURE 17

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE



Step 1: Use Figure 14 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_T = ... L × density (kg/L) ÷ 1000 = ... tonnes

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

Step 2: Observed or estimated

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

Step 3: Use Table

Condition = ...

Step 4: C = 0.03 g/m^3 for chlorine

10 × TLV® (1981)

Step 5: Computation required

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

Step 6: Use Figure 18

X = ... km

Step 7: Use Table

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

Step 8:

t = ... s

Step 9: Use Figure 20 with U from Step 2

X_t = ... km

FIGURE 18

CHLORINE

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE

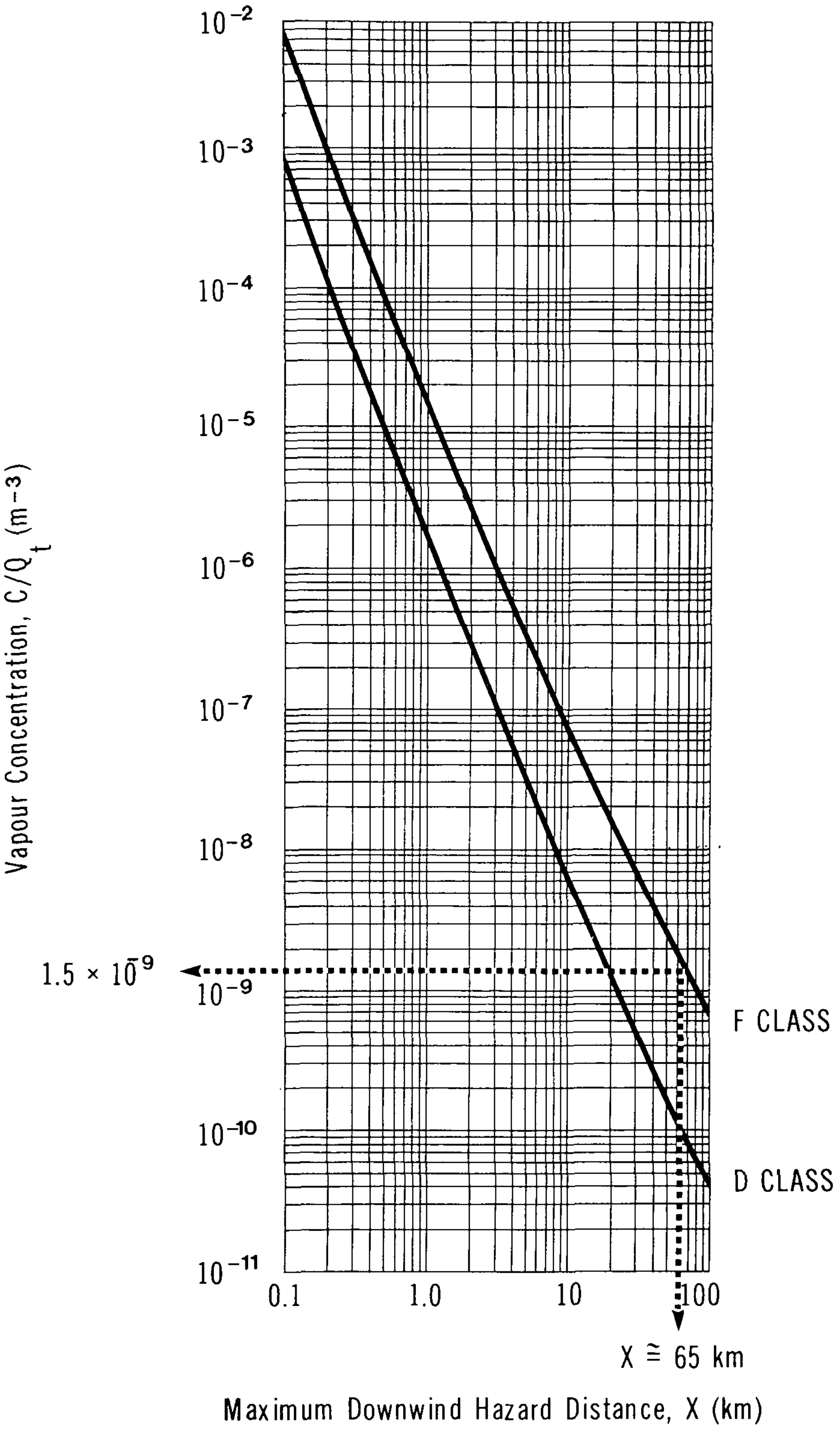


TABLE 9 WEATHER CONDITIONS

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

Use: The maximum hazard distance, X, downwind of the spill can be calculated from Figure 18 knowing:

- Q_T, the mass of vapour emitted (equivalent to liquid spilled)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value (TLV®, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3), which for a nonflammable vapour will be 10 x TLV®. Note: To convert the TLV®, in ppm, to a concentration in g/m^3, use Figure 19.

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.

5.3.2.2 Table 10: Maximum puff hazard half-widths. This table presents data on the maximum puff hazard half-width, $(W/2)_{max}$, for a range of Q_T values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the chlorine Threshold Limit Value (TLV®) of 0.003 g/m^3 (0.03 g/m^3).* The maximum puff hazard half-width represents the maximum half-width of the chlorine vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 10 is therefore only applicable for a chlorine hazard concentration limit of 10 x TLV® or 0.03 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

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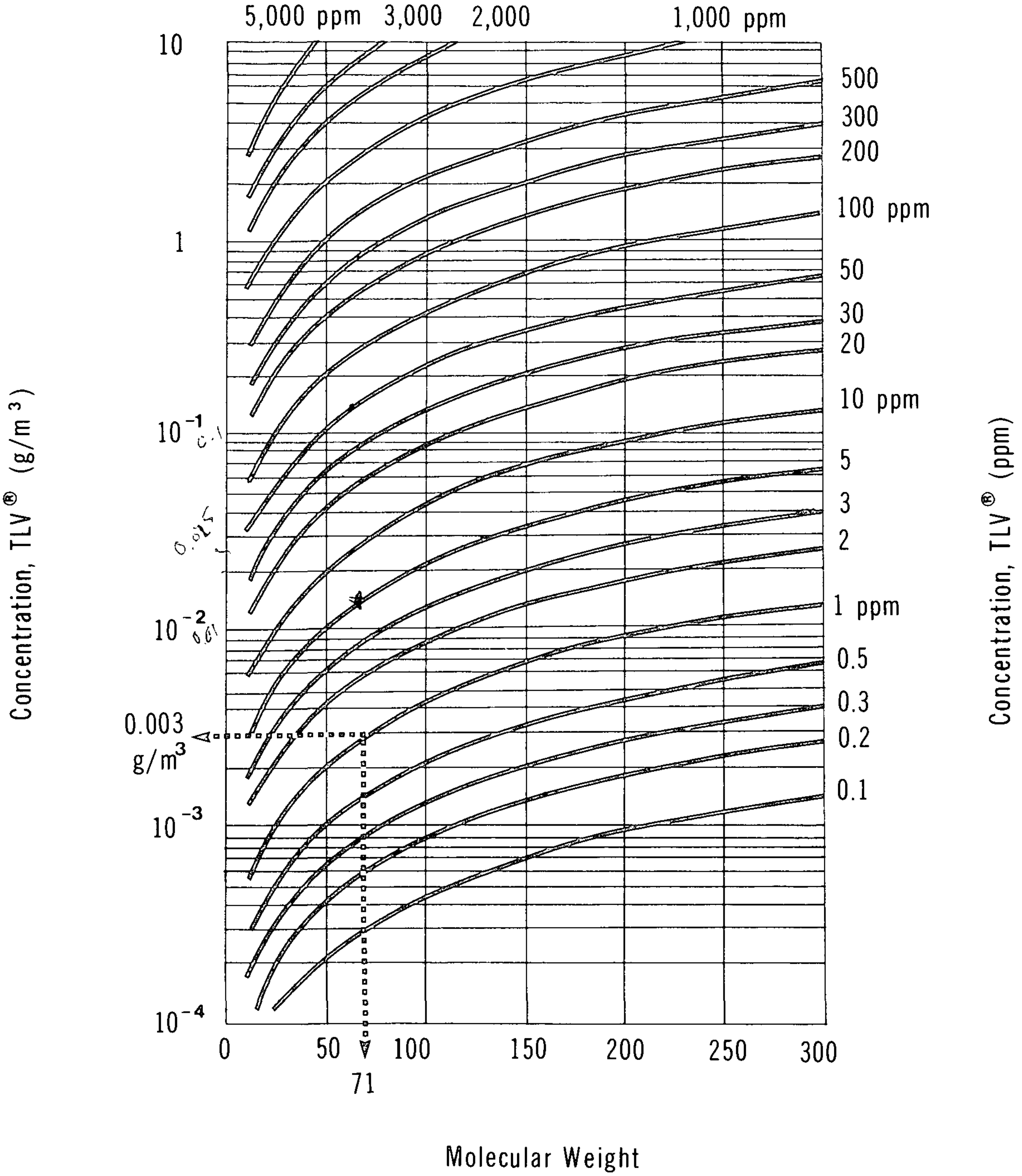
* Note that this is an arbitrary figure and that health effects have been reported for short-term exposure at lower concentrations (Section 7.4.1).

FIGURE 19

CHLORINE

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



Example: Chlorine , MW = 71, TLV® = 1 ppm, then TLV® in g/m³ = 0.003

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

TABLE 10 MAXIMUM PUFF HAZARD HALF-WIDTHS (FOR CHLORINE)

Weather Condition D			Weather Condition F	
Q_T (tonnes)	$(W/2)_{max}$ (m)		Q_T (tonnes)	$(W/2)_{max}$ (m)
950	4,000 (98.8 km)*		45	1,860 (99.5 km)*
900	3,920		25	1,450
800	3,750	Q_T = 20 tonnes →	20	1,315
700	3,560		15	1,165
600	3,360		10	980
500	3,130		7.5	865
400	2,875		5	730
300	2,580		2.5	540
200	2,205		1.5	435
100	1,695		1	375
75	1,515		0.75	335
50	1,300		0.5	285
25	1,000		0.25	220
20	916		0.1	150
15	820		0.05	115
10	705		0.01	60
7.5	640			
5	550			
2.5	425			
1.5	350			
1	305			
0.75	270			
0.5	235			
0.025	180			
0.1	130			
0.05	100			
0.01	55			

* The maximum plume distance at which the half-widths are valid

Example: Under weather condition F and Q_T = 20 tonnes, then puff hazard half-width $(W/2)_{max}$ = 1,315 m

Note: Above table is valid only for a chlorine concentration of 10 x TLV®, or 0.03 g/m^3.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of total vapour release quantities (Q_T) used was 0.01 to 950 tonnes, respectively. If the entire contents of an 80,000 L (17,600 Imp. gal.) tank car spill, the mass spilled would be 117,500 kg or approximately 118 tonnes. Therefore, under class D of Table 10, data are provided for up to 8 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of total vapour release quantities (Q_T) used was 0.01 to 45 tonnes. Therefore, under class F of Table 10, data are provided for only about 40 percent of a standard rail car load.

Use: Knowing the weather condition and Q_T, pick the closest value in the table and the corresponding $(W/2)_{max}$, the maximum puff hazard half-width, in metres. (For numbers not shown, interpolate Q_T and $(W/2)_{max}$ values.) Also, refer to the example at the bottom of Table 10.

5.3.2.3 Figure 20: Puff travel time versus travel distance. Figure 20 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

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

5.3.3 Sample Calculation. The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid chlorine. 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 quantity) in a particular spill situation if possible.

Problem

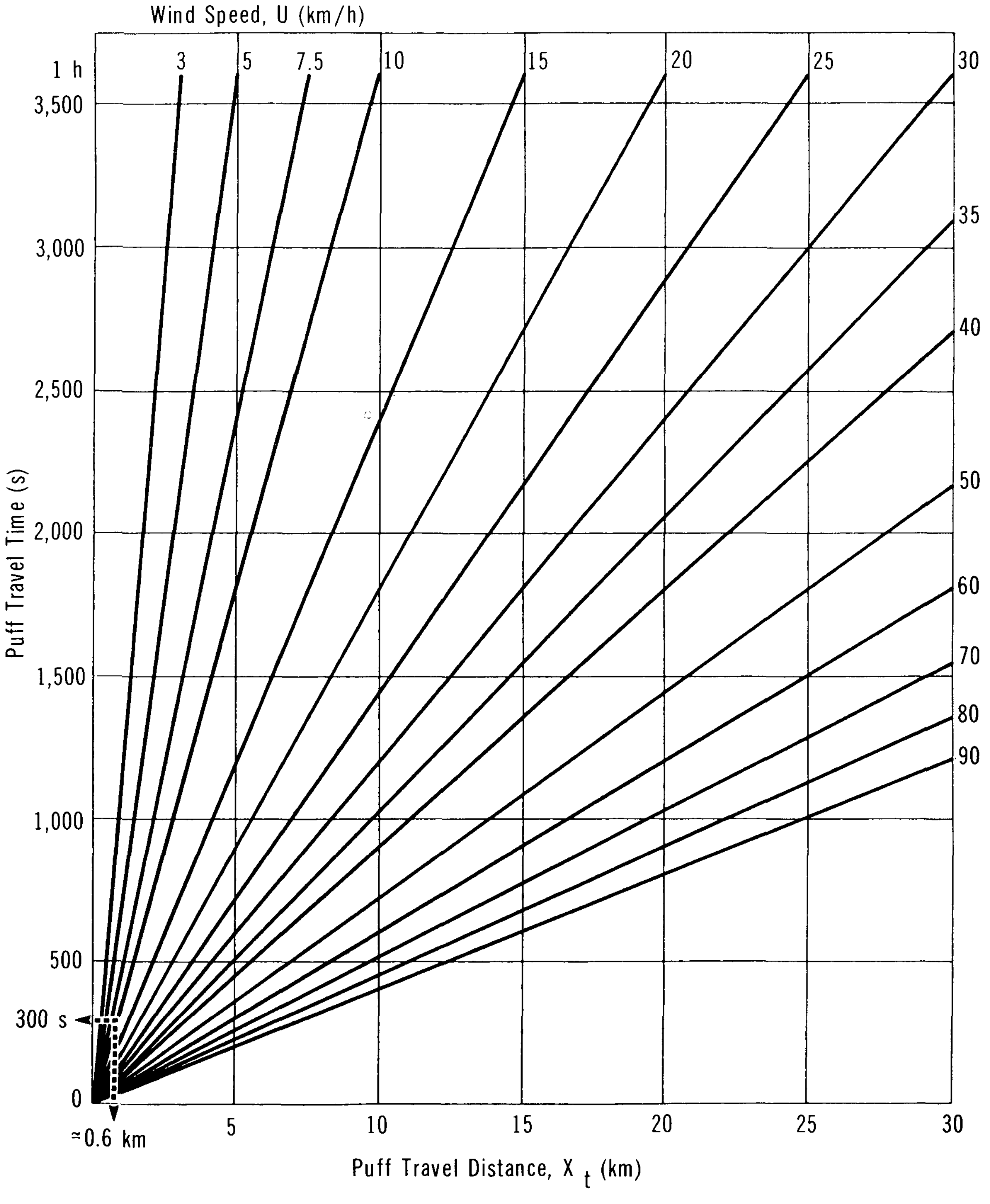
During the night, at about 2:00 a.m., 20 tonnes of liquid chlorine were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution:

Step 1: Quantity spilled is given

- $Q_T = 20$ tonnes or 20×10^6 g
- $Q_T = 2 \times 10^7$ g

PUFF TRAVEL TIME VS TRAVEL DISTANCE



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

- Use available weather information, preferably on-site observations
- Given: U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s
  D = NW or 315° (D = direction from which wind is blowing)

Step 3: Determine weather condition

- From Table 9, weather condition = F since U is less than 11 km/h and it is night

Step 4: Determine hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL; since chlorine vapours are not flammable, this is 10 x TLV®
  C = 0.03 g/m^3 (TLV® = 0.003 g/m^3; no LFL)

Step 5: Compute C/Q_T

- $C/Q_T = \frac{0.03}{2 \times 10^7} = 1.5 \times 10^{-9}\ \text{m}^{-3}$

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

- from Figure 18 with $C/Q_T = 1.5 \times 10^{-9}\ \text{m}^{-3}$ and weather condition F, X ≃ 65 km

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

- Use Table 10
- With Q_T = 20 tonnes
- Then for weather condition F, $(W/2)_{max}$ = 1,315 m

Step 8: Determine the time since spill

- t = 5 min x 60 = 300 s

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

- Using Figure 20 with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from X_t = Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 10: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (1,315 m) by the maximum hazard distance downwind of the instantaneous point source (65 km) along the direction of the wind, as shown in Figure 21
- 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 22

FIGURE 21

CHLORINE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

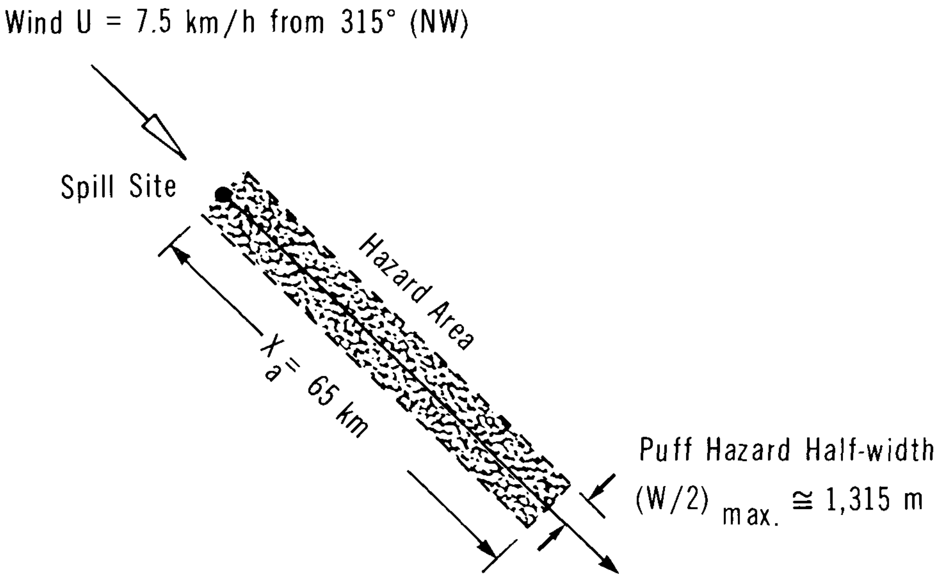
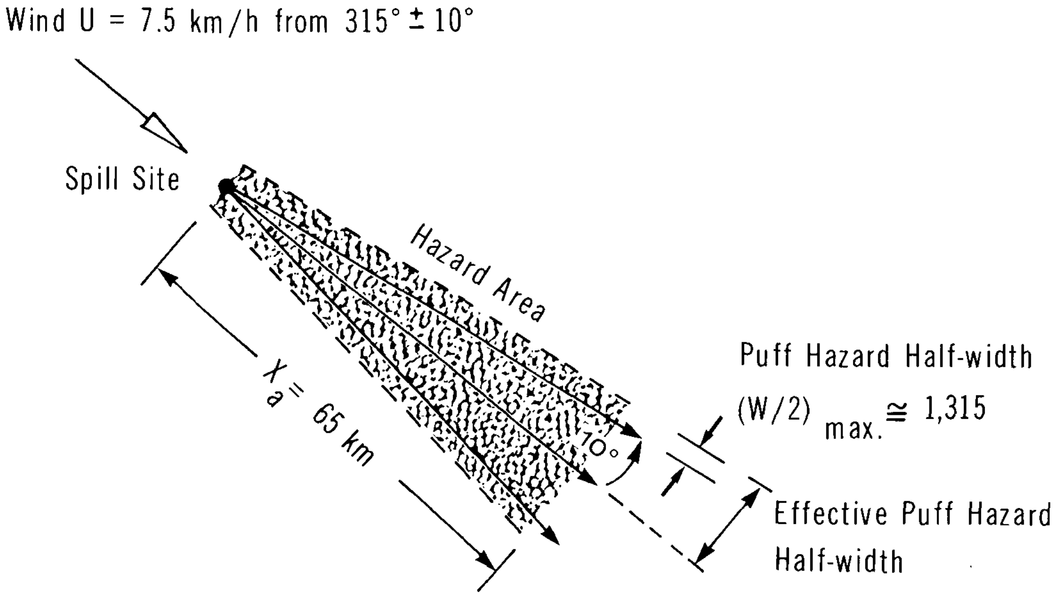


FIGURE 22

CHLORINE

HAZARD AREA FOR UNSTEADY WINDS , EXAMPLE PROBLEM



= X × 1000 × tan 10° + $(W/2)_{max.}$

= 65 × 1000 × tan 10° + 1,315 m

= 12,780 m

= 12.8 km

- Note that the puff has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h there remain 515 minutes (8 1/2 hours) before the puff reaches the maximum downwind hazard distance of 65 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled in water, liquid chlorine sinks and boils, producing a corrosive mixture of gaseous chlorine, chlorine hydrate, hypochlorous acid and hydrochloric acid, and a dangerous, visible vapour cloud. While its solubility in water is relatively low, chlorine represents a serious water pollution hazard because of its toxicity at low concentrations. Experiments show that seawater has a natural chlorine demand of about 1.5 mg/L in 30 min and twice that after 2 days. Addition of chlorine to seawater will have a marked effect on pH, EL, alkalinity and toxicity. However, dilution should result in the removal of the chlorine through redox reactions and a decrease of the alkalinity by only 2 percent (JHM 1977).

No modelling has been carried out for the complex heat and mass transfer reactions which occur when liquid chlorine is spilled in water. In the absence of better information, it is suggested that one half of the mass of any chlorine spill be assumed to dissolve in the watercourse or lake. This is approximately consistent with the data above. Considering the very low boiling point and relatively low solubility of chlorine in water, this assumption will likely overestimate the water pollution hazard.

When chlorine dissolves in water, 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. As chlorine is denser than water, the maximum concentration would be expected near the bottom.

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 24: time versus distance for a range of average stream velocities
Figure 25: hydraulic radius versus channel width for a range of stream depths
Figure 26: diffusion coefficient versus hydraulic radius for a range of average stream velocities
Figure 27: alpha* versus diffusion coefficient for various time intervals
Figure 28: alpha versus delta* for a range of spill sizes
Figure 29: maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 30: volume versus radius for the hazard zone for a range of lake depths
Figure 31: average concentration versus volume for the hazard zone for a range of spill sizes

The flow chart in Figure 23 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 24 through 29) are described in the following sub-sections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 24: Time versus distance. Figure 24 presents a simple relationship between average stream velocity, time and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be obtained readily from Figure 24.

Figure 25: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentrations is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream

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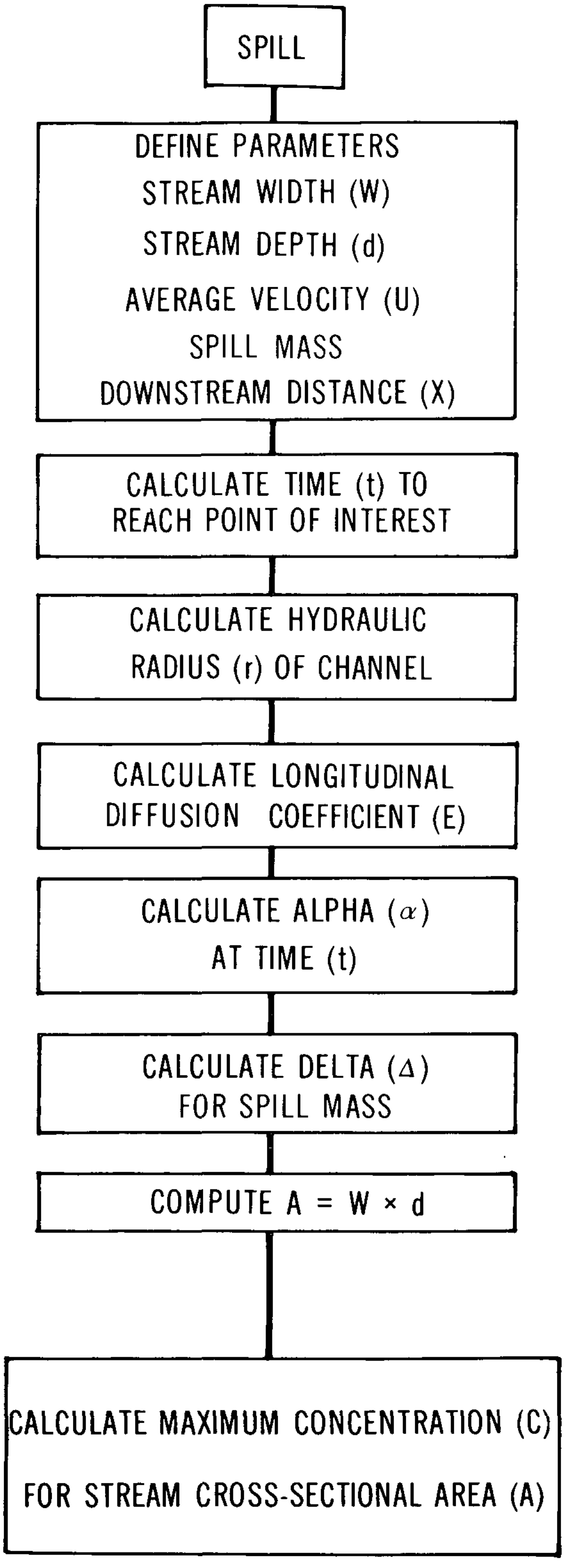
* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

FIGURE 23

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 24

t = __________ minutes

Step 3: Use Figure 25

r = __________ m

Step 4: Use Figure 26

E = __________ m

Step 5: Use Figure 27

α = __________

Step 6: Use Figure 28

Δ = __________

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

A = W × d ______ m^2

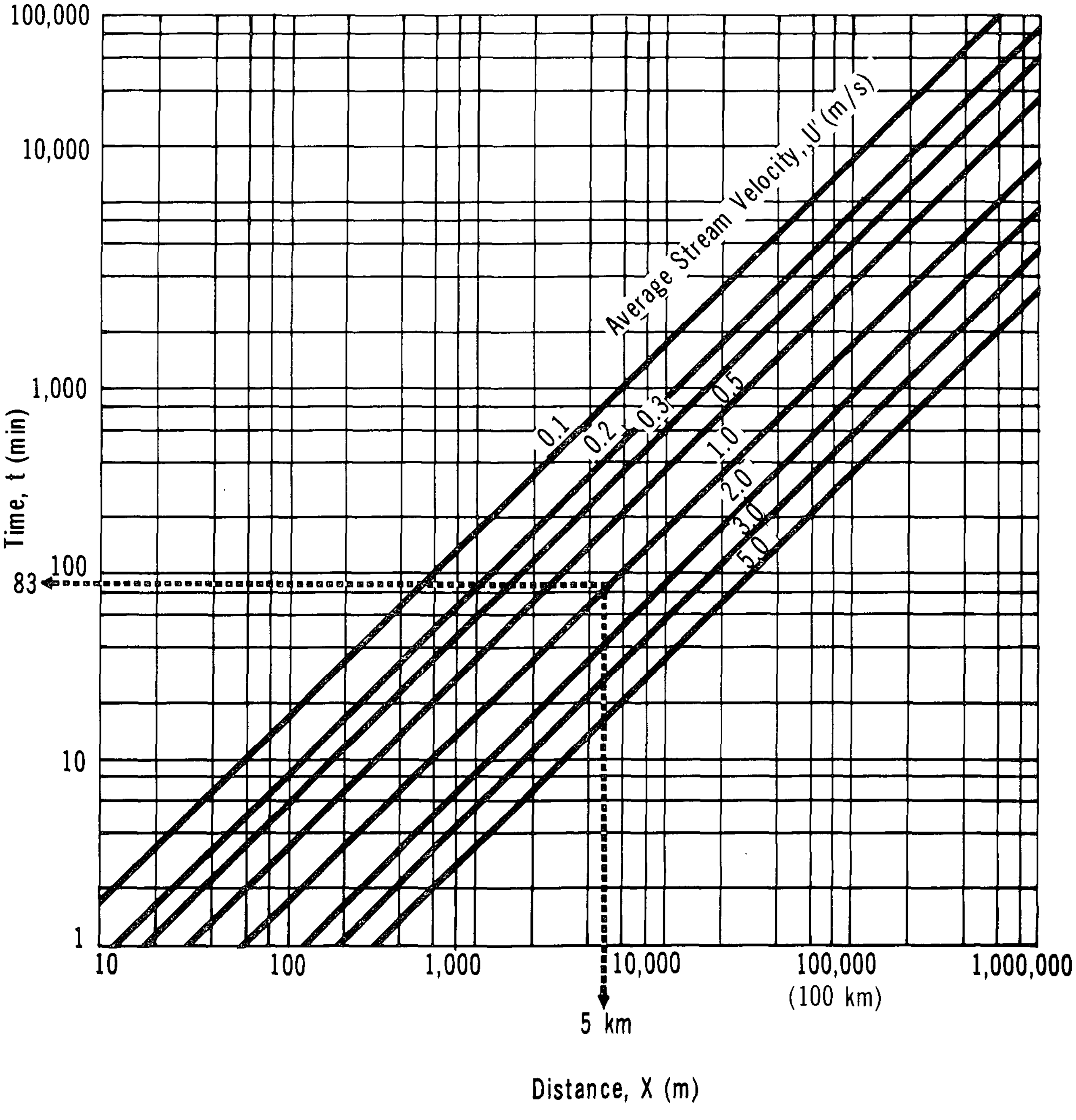
Step 8: Use Figure 29

C = __________ ppm

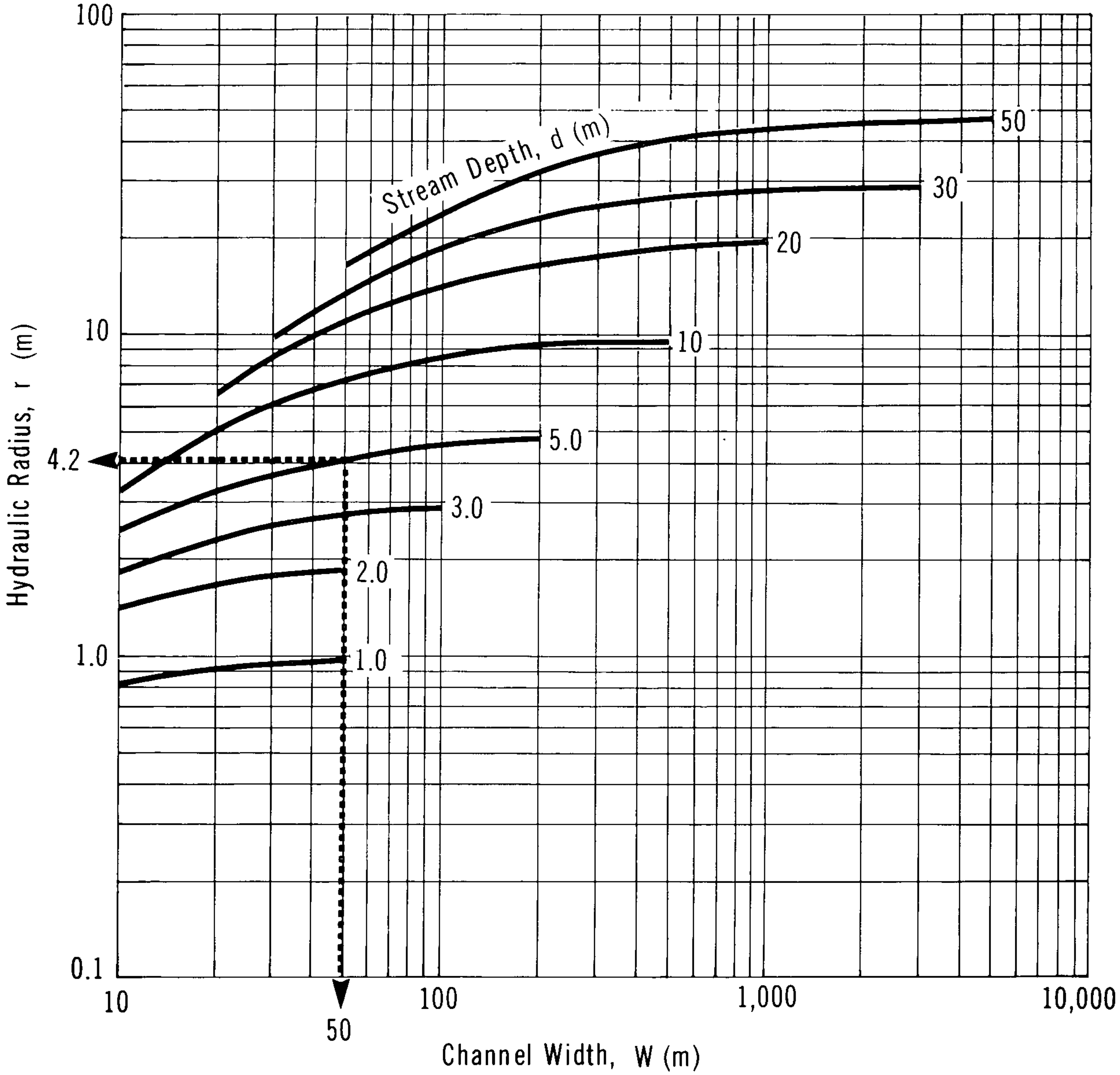
FIGURE 24

CHLORINE

TIME vs DISTANCE



HYDRAULIC RADIUS VS CHANNEL WIDTH



cross-sectional area (A) divided by the wetted perimeter (P). Figure 25 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 26: Diffusion coefficient versus hydraulic radius. Figure 26 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 25 and the average stream velocity (U).

Figure 27: Alpha versus diffusion coefficient. Figure 27 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 28: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 28 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 29: Maximum concentration versus delta. Figure 29 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 29 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 30: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 30. The radius (r) represents the distance from the spill to the point of interest.

Figure 31: 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 31 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.

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS

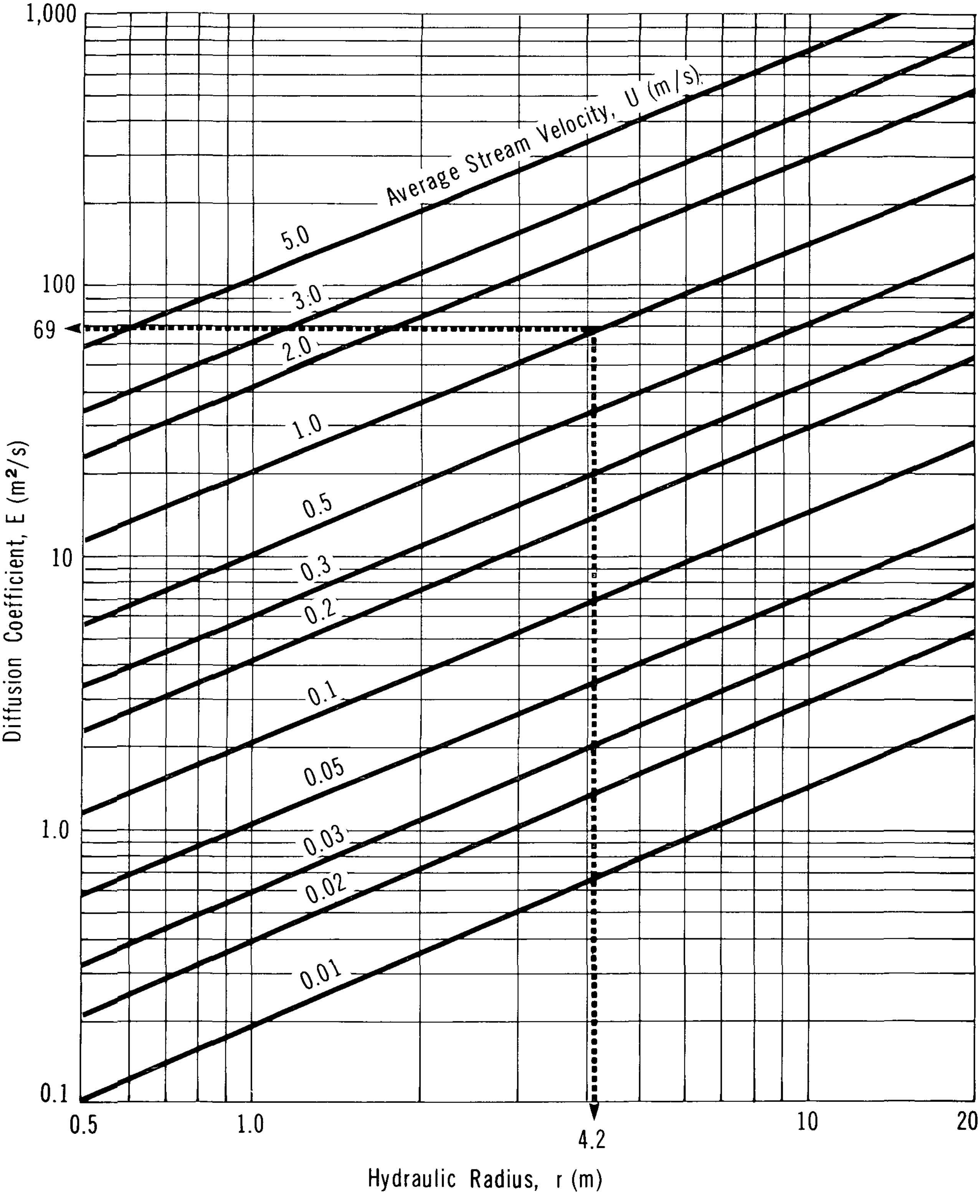


FIGURE 27

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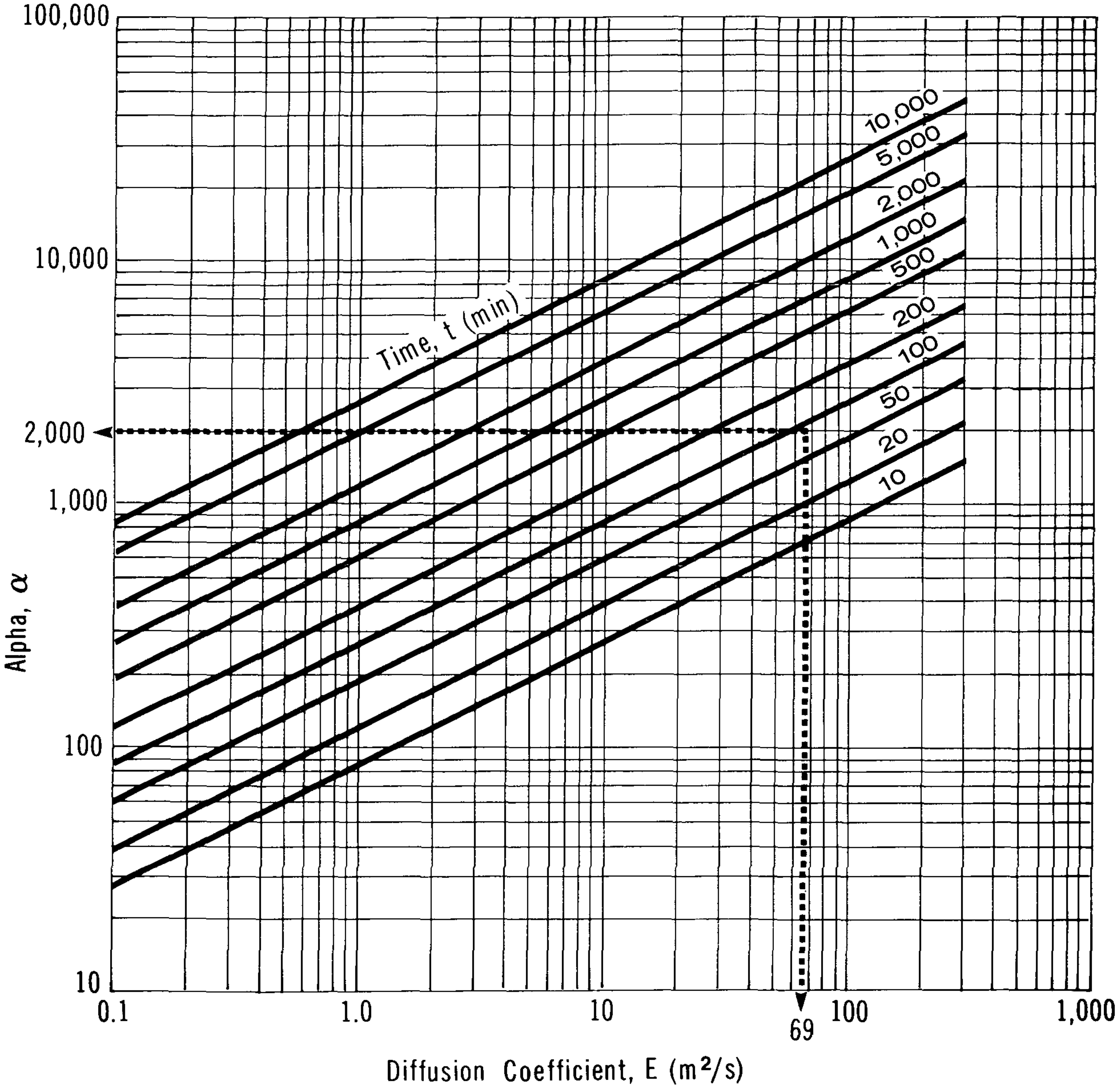
ALPHA vs DIFFUSION COEFFICIENT



CHLORINE

ALPHA vs DELTA

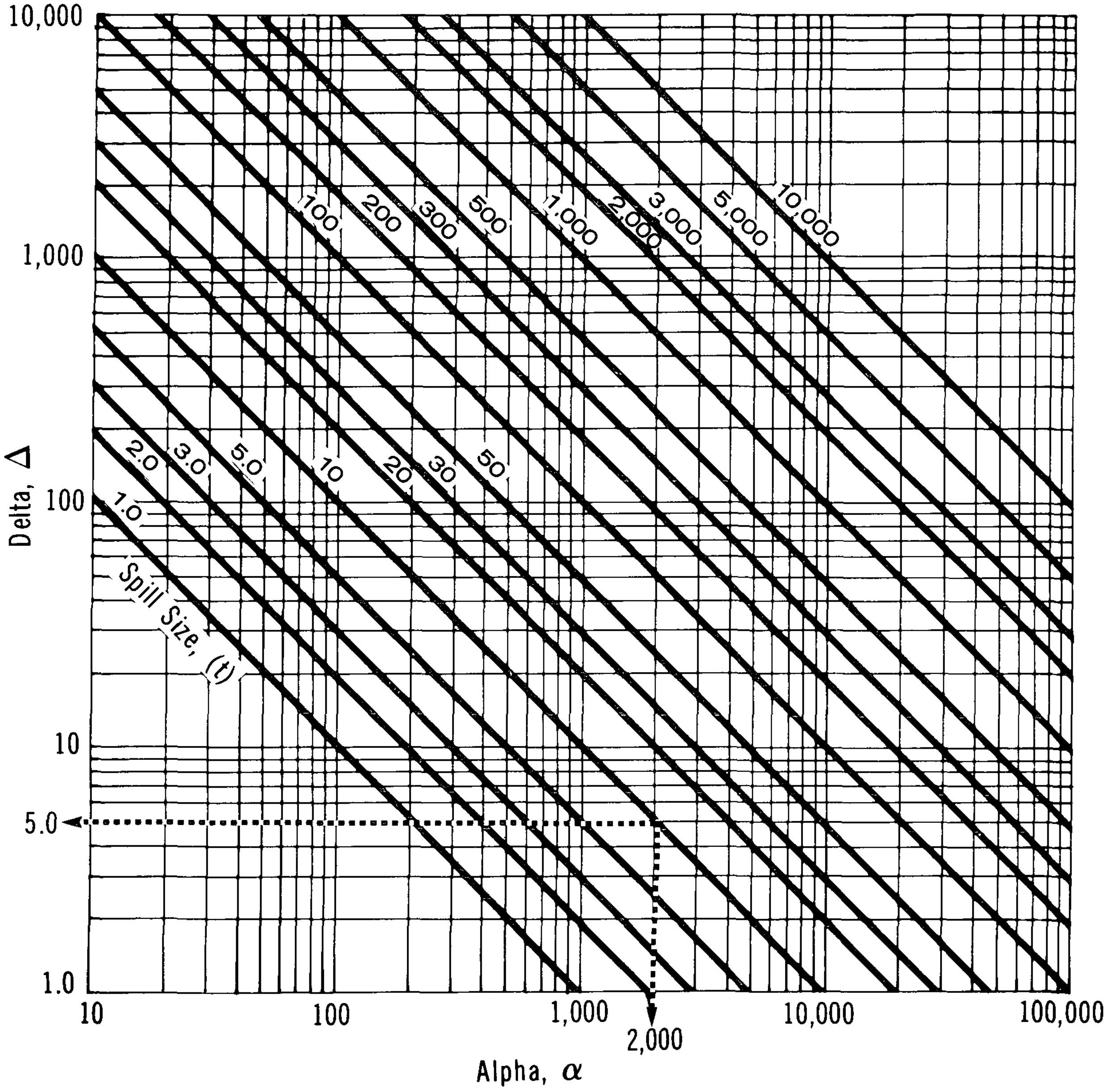


FIGURE 29

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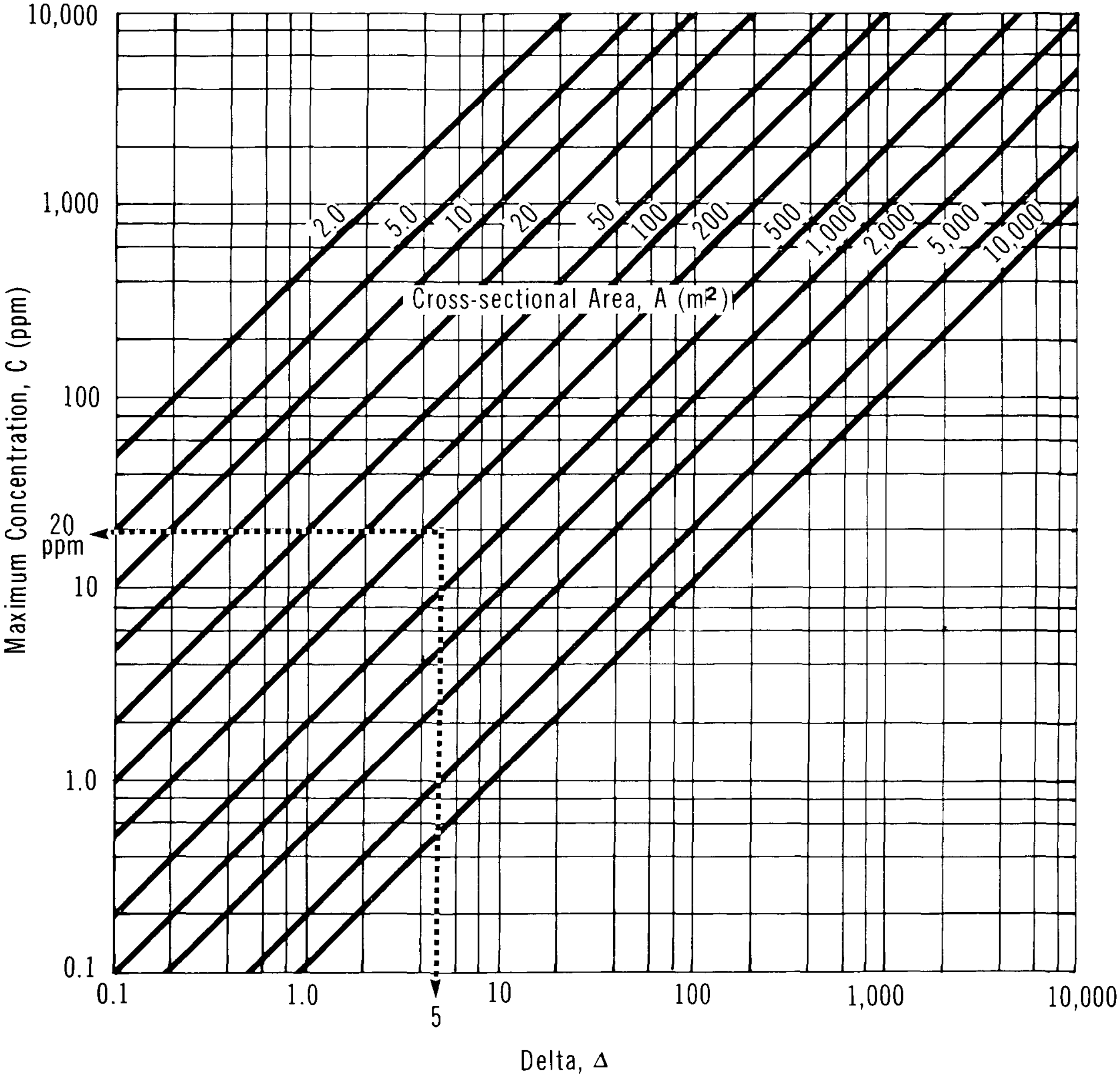
MAXIMUM CONCENTRATION vs DELTA



CHLORINE

VOLUME vs RADIUS

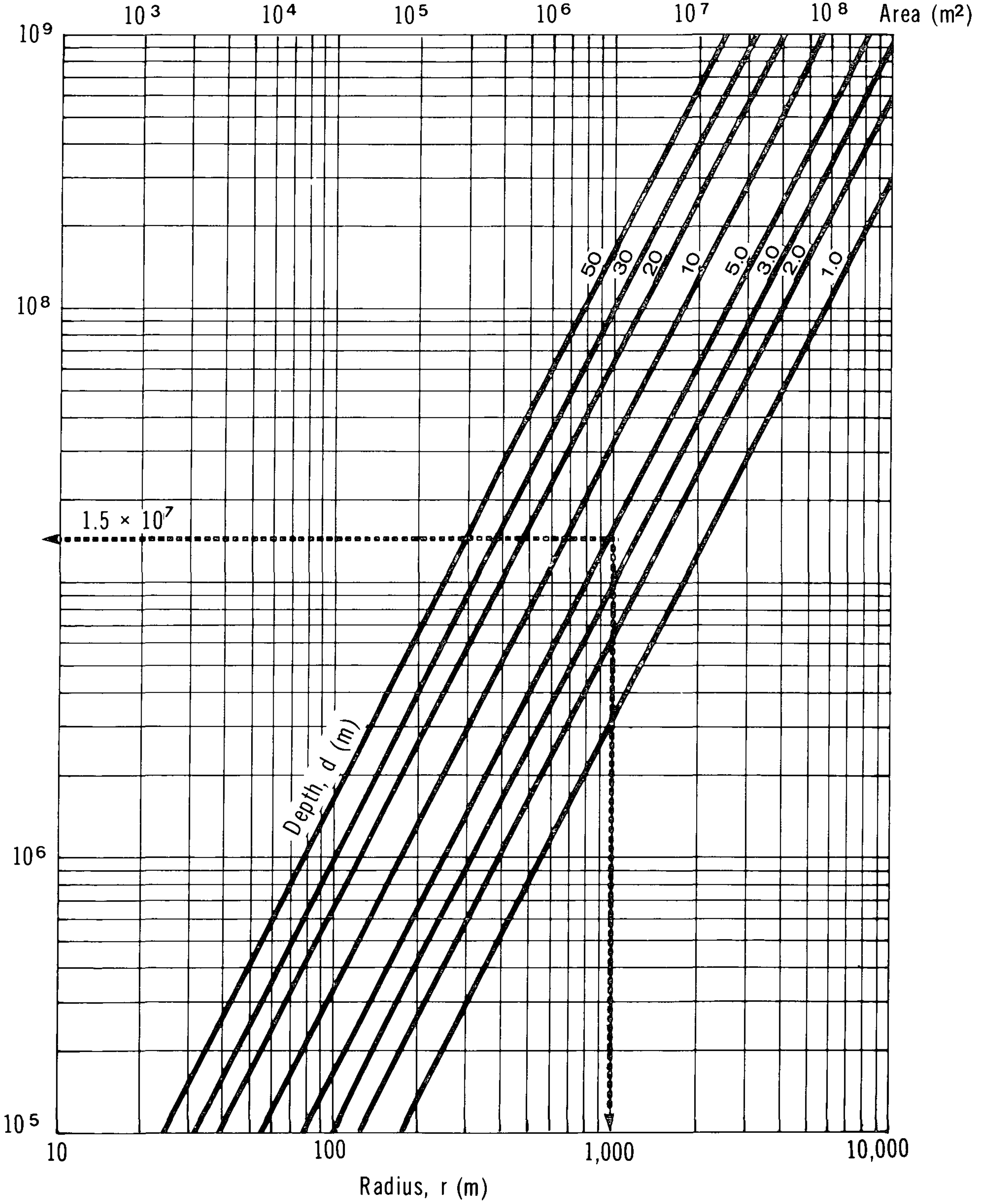
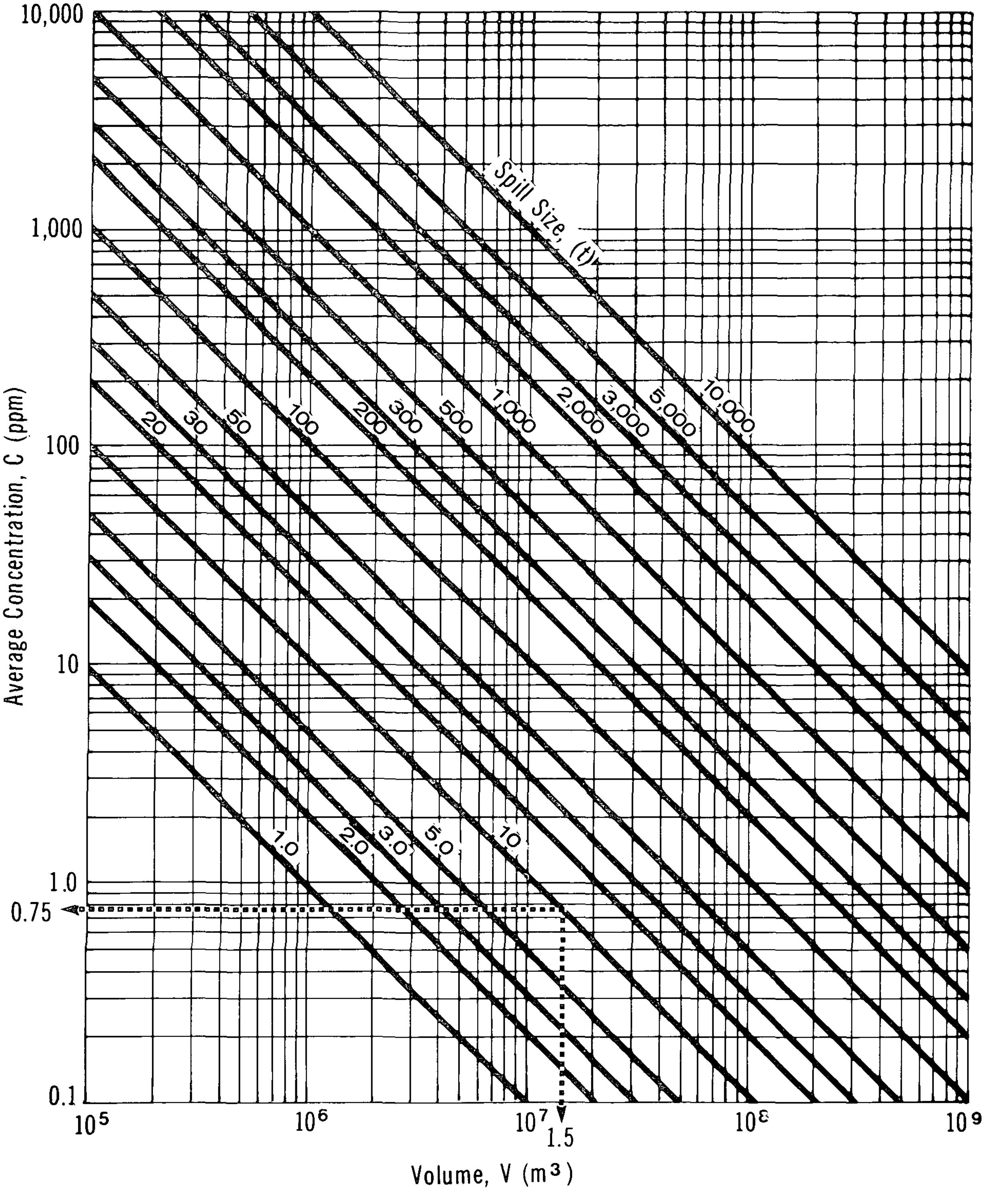


FIGURE 31

CHLORINE

AVERAGE CONCENTRATION vs VOLUME



5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal rivers. A 20 tonne spill of liquid chlorine 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 assuming that 50 percent of the chlorine is dissolved in water?

Solution

Step 1: Define parameters

- $W = 50$ m
- $d = 5$ m
- $U = 1$ m/s
- spill size = 10 tonnes of chlorine dissolved

Step 2: Calculate time to reach point of interest

- Use Figure 24
- With $X = 5{,}000$ m and $U = 1$ m/s, $t = 83$ min

Step 3: Calculate hydraulic radius (r)

- Use Figure 25
- With $W = 50$ m and $d = 5$ m, $r = 4.2$ m

Step 4: Calculate longitudinal diffusion coefficient (E)

- Use Figure 26
- With $r = 4.2$ m and $U = 1$ m/s, $E = 69$ m^2/s

Step 5: Calculate alpha (α)

- Use Figure 27
- With $E = 69$ m^2 and $t = 83$ min, $\alpha = 2{,}000$

Step 6: Calculate delta (Δ)

- Use Figure 28
- With alpha (α) = 2,000 and mass = 10 tonnes, delta (Δ) = 5

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

- $A = W \times d = 50 \times 5 = 250$ m^2

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

- Use Figure 29
- With $\Delta = 5$ and $A = 250$ m^2, $C = 20$ ppm

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of liquid chlorine has occurred in a lake. The point of interest is located on the shore approximately 1,000 m from the spill. The average depth of water between the spill site and the point of interest is 5 m. What is the average concentration of pollutant which could be expected assuming that 50 percent of the chlorine is dissolved?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1,000 m
- spill size = 10 tonnes (assumed dissolved)

Step 2: Determine the volume of water available for dilution

- Use Figure 30
- With r = 1,000 m, d = 5 m, the volume is approximately 1.6 x 10^7 m^3

Step 3: Determine the average concentration

- Use Figure 31
- With V = 1.6 x 10^7 m^3 and spill size = 10 tonnes, the average concentration is 0.72 ppm

5.5 Subsurface Behaviour: Penetration into Soil

Chlorine is shipped and stored primarily as liquified compressed gas. When a spill of this material occurs, it is exposed to atmospheric conditions and will therefore vaporize rapidly. As a result, the hazard potential to groundwater is minimal from a small spill, but more serious in the case of large spills.

A potential problem exists if precipitation occurs before the chlorine pool has completely vaporized or while substantial vapour is concentrated in low-lying areas. The precipitation will become acidified due to dissolution and the formation of hydrochloric and hypochlorous acids. The solution will infiltrate the soil and, under certain conditions, may reach the groundwater, acidifying it. The seriousness of this situation depends on specific soil conditions and location of groundwater. Consequently, no penetration nomograms have been prepared.

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water.

6.1.1.1 Canada. Chlorine levels in natural water used for drinking are not regulated, but trihalomethanes (reaction products) should not exceed 0.35 mg/L. The objective concentration of the latter is less than 0.005 mg/L (Guidelines/Canadian/Water 1978). The chloride objective is 200 mg/L (Water Management Goals 1978).

6.1.1.2 Other. United States, France and Bulgaria's limit for chloride in domestic water is 250 mg/L. The limit for Tanzania is 800 mg/L. The European WHO (World Health Organization) limit is 600 mg/L. The International WHO acceptable and allowable limits are 200 mg/L and 600 mg/L, respectively (Jorgensen 1979).

6.1.2 Air. Ontario has specified an emission limit of 300 µg/m^3 chlorine in air (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Chlorine has been assigned a TL_m96 (4-day median lethal toxicity rating) of less than 1 mg/L (RTECS 1979).

In the United States, 3 µg/L has been recommended for protection of freshwater aquatic life, with a short-term limit of 50 µg/L for a period of up to 1/2 hour in every 24-hour period (WQC 1972).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Kill Data					
2.2	not stated	Bluefish	killed; broken backs	James River; Virginia	Bellanca 1977
0.3	2	Trout	killed		WQC 1963
1.0	1	Trout	killed		WQC 1963
0.8	4	Golden shiners	killed		WQC 1963

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Fish Toxicity Tests</u>					
0.07 (total residual chlorine, TRC)	96	Channel catfish (fingerling)	LC_{50}; gill sodium uptake drastically impaired	flow through bioassay	Hammond 1979
0.23; 0.28 (TRC)	30 min	Emerald shiner (yearling; adult)	LC_{50}	Lake Superior water; 25°C	Fandrei 1979
0.2	not stated	Fish	LD_{50}		Jorgensen 1979
0.17	24	Goldfish	TL_m	intermittent chlorination, 17 to 25.5°C	Dickson 1977
0.44	96	Bluegill	LC_{50}; distress	intermittent chlorination, 15°C	Bass 1977
0.1	96	Fathead minnow	TL_{50}		Brungs 1973
0.88	1	Yellow perch	LC_{50}		Brungs 1973
0.74	1	Large mouth bass	LC_{50}		Brungs 1973
0.08	168	Rainbow trout	TL_m		WQC 1963
0.08	18	Brook trout	mean survival time		WQC 1963
3.0	24	Green sunfish	28% killed		WQC 1963
0.15 to 0.2	12 to 16 days	Carp	25% killed		WQC 1963
<u>Microorganisms</u>					
0.5	not stated	*E. coli* (waterborn)	injury to cells; decrease in respiration		Camper 1979
1.45	2	Protozoa	53% killed (3 Cl_2 additions); 94% killed (7 Cl_2 additions)	intermittent chlorination; Douglas Lake, Mich.	Dickson 1977
0.5	72	Daphnia	killed	soft	WQC 1963

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Invertebrates					
0.5	100	Larval clam	100% mortality		Hall 1981
8 (TRC)	not stated	Leech	decreased respiration		Osborne 1980
1	3	*Nais* sp.	lethal	hard	EPA 440/9-75-009
1	not stated	Minute crustacea	killed		WQC 1963
2.5	not stated	Mussels, snails, sponges	killed		WQC 1963

Conc. (mg/L)	Time (hours)	Species	Result	Reference
Zooplankton				
0.019	4	*Keratella cochlearis* (rotifer)	TL_{50}	Hall 1981
0.49	96	*Daphnia pulex*	LC_{50}	Hall 1981
0.017	46	*Daphnia magna*	LC_{50}	Hall 1981

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Amphibians					
2	12	Bullfrog tadpoles	lethal	24°C	Pimental 1971
3.8	48	Tadpoles	no mortality		WQC 1963

Conc. (mg/L)	Species	Result	Reference
Microflora			
0.25 to 3.0	Algae	controlled	WQC 1963
56 to 10	Synura	killed	WQC 1963

6.2.2.2 Saltwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxicity Tests					
208 µg/L	1	Coho salmon	LC_{50}	13°C	Stober 1980
15% effluent (v/v)	not stated	Shiner perch	acutely toxic	Puget Sound, Washington (sewage discharge)	Dinnel 1979
0.5% effluent	not stated	English sole	chronically toxic	Puget Sound, Washington (sewage discharge)	Dinnel 1979
0.002	not stated	Coho salmon	avoidance		Stober 1978
0.14	24	Ocean spot	TL_m; stress	York Rv., Virginia	Bellanca 1977
1 to 10	not stated	Marine fish (shiner perch)	slight to extreme irritation		WQC 1963
Invertebrates					
0.22	96	Grass shrimp	TL_m	York Rv., Virginia	Bellanca 1977
<0.005	48	Copepods, oysters, clam larvae	TL_m; affect oyster production	York Rv., Virginia	Bellanca 1977
10	4 h/day	Barnacles	killed		WQC 1963
0.01 to 0.05	not stated	Oysters	reduced activity		WQC 1963
1	not stated	Oysters	pumping stops		WQC 1963
Plants					
0.5	not stated	Diatom	thermal shock; death	39°C	Maggi 1980
0.5	not stated	Flagellate	delays development; thermal shock	24°C	Lassus 1980
4	not stated	*Pavlova lutheri*	LD_{50}		Videau 1979

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Plants (cont'd)					
0.6	not stated	*Phaeodactylum tricornutum* (diatom)	reduced or ceased growth		Videau 1979
5	120	Giant kelp	10-15% reduction in photosynthesis after 2 days and 50-70% after 5-7 days		WQC 1963

6.2.3 Aquatic Studies.

6.2.3.1 Freshwater. In studies done in rivers in Virginia, chlorinated wastewater effluent has been proven to be highly toxic to the aquatic environment and to result in major fish kills (Bellanca 1977). Toxicity to aquatic life generally depends on the available chlorine in the effluent which in turn depends on the chlorine dose rate and the chlorine demand.

In another study, chlorination resulting from power plants was shown to have an adverse effect on phytoplankton (e.g., algae, primary producers of the food chain) and zooplankton (primary consumer level of the food chain). Percent mortality of the populations of these two organisms is similar as their generation times are of days or hours compared to aquatic invertebrates and fish which have generation times of weeks or years (Hall 1981).

Other studies have shown that addition to wastewater effluent of the minimum dose of chlorine for disinfection can be effective in protecting aquatic organisms during their critical life stages (Bellanca 1977).

Long-term exposure of chlorine to channel catfish has been found to drastically reduce both blood pressure and heart rate. These changes are indicative of a stressful environment (Hammond and Bishop 1979).

6.2.3.2 Saltwater. The toxicity of chlorine to estuarine organisms appears to be similar to that of freshwater organisms (Bellanca 1977).

Effects of sewage discharges, from a number of sewage treatment plants to seawater, have been studied. Major reductions in fish life and species diversity below the outfalls were found. No fish were found in water with a total chlorine content of

0.37 mg/L. The species diversity index was 0 at 0.25 mg/L. Turbidity was also found to have a major impact (Dinnel 1979).

In one study, low-level chlorination was found to lead to significant shifts in the species composition of marine phytoplankton communities. The shifts depend on (a) the composition of the communities at the time of stress, and (b) morphological and systematic characteristics of species, thus exhibiting different sensitivities to chlorine. Chlorine has an impact similar to that demonstrated with other pollutants: a decrease in the predominance of centric diatoms and subsequent success of pennate diatoms and microflagellates. Very low concentrations of chlorine (0.05 to 0.15 mg/L) have caused changes in species composition (Sanders 1980).

6.3 Toxicity to Other Biota

6.3.1 Mammals. The LC_{LO} rating for mammals (inhalation mode) is 500 ppm for 5 minutes (RTECS 1977).

Laboratory mice have grown to adulthood with no ill effects from drinking water containing 100 and 200 mg/L free available chlorine (WQC 1963).

6.3.2 Plants. In one study, it was shown that irrigation water containing 50 mg/L or less of residual chlorine did not impair the growth of land plants: 100 to 150 mg/L injured some plants but did not affect others; and 500 to 1,000 mg/L killed plant tops and roots (MHSSW 1976).

Chlorine gas is found to accumulate in the leaves after entering via the stomata. Damage depends on exposure time, species, and concentration of gas (Pigulevskaya 1980).

6.4 Effect Studies

Bacterial toxicity of chlorine is mostly due to undissociated hypochlorous acid (HOCl). At a lower pH, the proportion of HOCl will be higher and toxicity will increase. The toxicity is also highly dependent on temperature, dissolved oxygen, and synergism or antagonism of other dissolved materials, notably ammonia. Chlorine and ammonia form toxic chloramines; chlorine itself is somewhat more toxic than monochloramine (OHM-TADS 1981; EPA 440/9-75-009).

6.5 Degradation

6.5.1 Chemical Degradation. Because chlorine is so reactive, it is not persistent; it is ultimately reduced to chloride ion (OHM-TADS 1981). Chlorination studies conducted on natural and artificial seawater have shown two phases of chlorine losses in seawater: a rapid initial loss followed by a continuous loss at a sharply reduced rate. The initial loss reaches a saturation level that varies widely between natural seawater samples and appears to be related to a true organic demand. Losses continue over a period of 10 days and are pronounced in seawater containing bromine. Other studies have indicated that the loss of chlorine is associated with the bromine chemistry system in seawater. The fate of the lost chlorine was not determined (Goldman 1979).

The presence of light, even in intensities of only a few percent of full mid-day sun, may significantly affect both the rate and mechanism of the dissipation of chlorine in seawater. Light increases the rate of dissipation of hypobromite formed from the added chlorine. Bromate is also a product formed when chlorinated seawater is exposed to light, and its rate of formation increases with increasing light intensities (Wong 1980; JHM 1977). The chemistry of chlorine in seawater is quite complex and is explained in detail in the above reference.

6.5.2 B.O.D. Studies of chlorine residues have been shown to profoundly affect B.O.D. (biological oxygen demand) over a certain length of time. Chlorine concentrations of > 0.01 ppm were found to totally abolish the B.O.D. (Kaneko 1980).

6.6 Long-term Fate and Effects

No potential for bioaccumulation or bioconcentration has been cited. However, from the studies evaluated, an assessment of potential bioaccumulation and biological magnification of chlorinated organic compounds by all trophic levels (aquatic) is required (Hall 1981).

7 HUMAN HEALTH

There is a considerable amount of information in the published literature concerning the toxicological effects in test animals due to inhalation of chlorine, in addition to studies detailing human response to exposure.

No evidence was found to indicate that chlorine is a potential human carcinogen; however, mutagenic effects have been observed in the genetic material of bacteria.

TOX TIPS (a summary of current research activity) describes only one recent animal study planned for chronic exposure involving Fischer 344 rats. It was begun in 1981.

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

7.1 Recommended Exposure Limits

The exposure standards for chlorine are based upon its corrosive properties. 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	1 ppm (3 mg/m^3)	TLV 1983
TWA (8 h)	USA-OSHA	1 ppm (3 mg/m^3)	NIOSH/OSHA 1981
MIC	USSR	0.3 ppm (1 mg/m^3)	ILO 1980
TWA	Switzerland	0.5 ppm (1 mg/m^3)	ILO 1980
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	3 ppm (9 mg/m^3)	TLV 1983
Ceiling (15 min)	USA-OSHA	1 ppm	NIOSH Guide 1978
PEL (15 min)	USA-NIOSH	0.5 ppm (1.5 mg/m^3)	NIOSH Guide 1978
Other Human Toxicities			
IDLH	USA-NIOSH	25 ppm (75 mg/m^3)	NIOSH Guide 1981
LC_{LO} (30 min)		873 ppm	RTECS 1979
TC_{LO}		15 ppm	Patty 1981

Inhalation Toxicity Index

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

$$\text{ITI} = 1{,}315.12\ (\text{Vapour Pressure, in mm Hg})/(\text{TLV}^{\circledR}\text{, in ppm})$$

$$\text{ITI} = 1{,}315.12\ (589.2\ \text{kPa @ } 21^{\circ}\text{C})/1\ \text{ppm}$$

$$\text{ITI} = 5.8 \times 10^{6}$$

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
High level (gas)	Caused burns around the mouth	Stout 1935. IN NIOSH 1976
Liquid (contact)	Will burn skin and eyes	CHRIS 1978
Liquid (contact)	Will cause frostbite	CHRIS 1978

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Liquid	Will burn skin and eyes	CHRIS 1978

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: Choking, pungent and irritating, bleach-like odour (AAR 1981)

Odour Index: 54,446 (AAR 1981)

Parameter	Media	Concentration	Reference
Threshold of Discomfort	In air	15.1 ppm	Fieldner et al. 1921. IN NIOSH 1976
Upper Recognition Threshold	In air	5 ppm	AAR 1981

Parameter	Media	Concentration	Reference
Median Recognition Threshold	In air	3 ppm	AAR 1981
Odour Threshold	In air	0.3 to 0.4 ppm	Ryazahov 1962. IN NIOSH 1976
Absolute Odour Threshold	In air	0.314 ppm	AAR 1981

7.3.2 Taste.

Parameter	Media	Concentration	Reference
Detection	In water	0.05 mg/L	ASTM 1980
-	In water	5.2 ppm	ASTM 1980
-	In coffee	108 ppm	ASTM 1980

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
1,000 ppm	Fatal after a few breaths	Braker 1977
833 ppm (30 to 60 min)	Death	Braker 1977
430 ppm (30 min)	LC_{LO}	RTECS 1979
40 to 60 ppm (30 to 60 min)	Pulmonary edema	Hedges 1979
30 ppm (min)	Choking, coughing, burning sensation	Hedges 1979
15.1 ppm	Minimum concentration producing irritation in the throat	Fieldner et al. 1921. IN NIOSH 1976
15 ppm (min)	Eye, nose and throat irritation	Hedges 1979
4 ppm (1/2 to 1 h)	No ill effects noted	Hedges 1979
3.5 to 4 ppm (16 min)	Nasal congestion. Tolerance limit. Coughing lasted 18 hours	Matt 1889. IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
2.5 ppm (5 min)	Burning eyes, mouth and throat	Matt 1889. IN NIOSH 1976
1.3 ppm (30 min)	Shortness of breath, headache	Patty 1981
1.3 ppm (7 min)	Eyes burning	Matt 1889. IN NIOSH 1976
1 ppm	Minimum effect level	Matheson 1980
1 ppm	Burning eyes, dry throat, coughing, difficulty in inhaling	Patty 1981
1 ppm (20 min)	Dull sensation in teeth, slight metallic taste, headache, burning of conjunctiva, skin, distinct taste, coughing, constriction of breathing	Beck 1959. IN NIOSH 1976
<1 ppm	Acute obstructive ventilatory defects clearing within 24 to 48 hours	Beck 1959. IN NIOSH 1976
0.5 ppm	Nasal irritation, coughing	NIOSH Guide 1981
0.5 ppm	One subject was accidentally exposed due to the use of a poor fitting respirator. Several hours later, victim developed mediastinal emphysema	Monts and Woodall 1944. IN NIOSH 1976
0.5 ppm	Optical chronaxie increased	Ryazanov 1962. IN NIOSH 1976
0.452 ppm	Burning of conjunctival tissue	Rupp and Henschler 1967. IN NIOSH 1976
0.2 ppm	Dry throat, slight cough, sensations in conjunctiva	Beck 1959. IN NIOSH 1976
0.058 ppm	Tickling in the throat	Rupp and Henschler 1967. IN NIOSH 1976
0.027 ppm	Tickling in the nose	Rupp and Henschler 1967. IN NIOSH 1976
Acute accidental exposure, unspecified concentration		
(After 1 to 3 wk)	Exertional dyspnea, easy fatiguability, cough and reduced lung volumes were noted	Kowitz et al. 1967 IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
(After 60 d)	Reduced lung volumes and oxygen levels were recorded. Acute alveolo-capillary injury	Kowitz et al. 1967. IN NIOSH 1976
(After 180 d)	Total lung capacity still reduced. Mean vital capacity reduced. Mean airway resistance increased. Arterial hypoxemia present	Kowitz et al. 1967 IN NIOSH 1976
SPECIES: Mammal		
500 ppm (5 min)	LC_{LO}	RTECS 1979
SPECIES: Dog		
2,000 to 50 ppm (30 min)	First showed general excitement, restlessness, barking, urination, defacation. Blinking of eyes, sneezing, copious salivation, retching, vomiting. Later frothed at the mouth, with laboured respiration. At 800 ppm, 50% of animals died within 3 days. At 900 ppm, 87% died within 3 days	Underhill 1920. IN NIOSH 1976
2,000 to 50 ppm (30 min)	Severe injury to mucous membranes of upper respiratory tract, irregular dilation and contraction of bronchi, patches of acute emphysema and atelectasis, inflammation, evidence of pneumonia in dogs dying within 24 hours. Dogs dying 2 to 5 days after gassing showed lobular pneumonia, abscesses, gangrene, bronchiolar spasm. Animals surviving 15 to 193 days after gassing showed emphysema, exudate in bronchioles consisting of fibroblasts, blood vessels with mononuclear cells	Winternitz 1920. IN NIOSH 1976
900 to 800 ppm (30 min)	At least 85% of animals died. In 20 dogs, temperature drop of 1°C per half hour for 2 hours, then more gradual	Barbour 1919. IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
	decline until death. Animals were unable to regulate body temperature when exposed to moderately high temperatures (35 to 40°C) or room temperature	
800 ppm (30 min)	LC_{LO}	RTECS 1979
800 ppm (2 to 7 h)	Rapidly increasing acidosis occurs	TDB (on-line) 1982
650 ppm (30 min) and never less than 280 ppm	Dogs rarely die	TDB (on-line) 1982
200 to 180 ppm (30 min)	Decrease in temperature of 0.7°C on average, in three dogs. Hypothermia lasted 6 hours on average. Irritant effects similar to those at 24 to 30 ppm, followed by general depression of muscle activity and dyspnea. No evidence of bronchitis or edema. Animals apparently normal after a few hours removal from exposure	Barbour 1919. IN NIOSH 1976
30 to 24 ppm (30 min)	Increase in body temperature of 0.8°C on average lasting 3 to 24 hours during gassing of four dogs. Chemical signs of irritation, lacrimation, salivation, mild retching, vomiting. Return to apparent normal after removal from exposure	Barbour 1919. IN NIOSH 1976
SPECIES: Cat		
660 ppm (4 h)	LC_{LO}	RTECS 1979
300 ppm (1 h)	May cause death after a period during which the conjunctiva is inflammed and there is coughing and dyspnea	TDB (on-line) 1982
200 to 100 ppm	Reflex constriction of bronchi lasting approximately 1 minute. Rate of respiration increased concomitantly	Gunn 1920. IN NIOSH 1976
138 ppm (1 h)	LC_{LO}	ITII 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
660 ppm (4 h)	LD_{LO}	RTECS 1979
200 to 100 ppm	Reflex constriction of bronchi lasting approximately 1 minute. Rate of respiration increased concomitantly	Gunn 1920. <u>IN</u> NIOSH 1976
SPECIES: Guinea Pig		
200 ppm (15 to 30 min)	Severe injury to mucous membranes of upper respiratory tract, irregular dilation and contraction of bronchi. Patches of acute emphysema and atelectasis, inflammation. Animals surviving 15 to 193 days after gassing showed emphysema, exudate in bronchioles consisting of fibroblasts, blood vessels with mononuclear cells	Faure et al. 1970. <u>IN</u> NIOSH 1976
SPECIES: Rat		
293 ppm (1 h)	LC_{50}	RTECS 1979
9 ppm	50% decrease in respiratory rate	Kane 1979
<u>Chronic Exposures</u>		
SPECIES: Human		
46 to 5 ppm	Caused corrosion of the teeth in workers chronically exposed	TDB (on-line) 1981
15 to 0 ppm (years)	Chronic poisoning	Doc. TLV 1981
7 to 0 ppm	Slight adverse effect on respiratory ailments	Doc. TLV 1981
6 to 3 ppm	Stinging or burning sensation in the eyes, nose, and throat; headache	Patty 1981
6 to 3 ppm	Causes sensation of stinging and burning of eyes in some individuals, with associated blepharospasm, redness and	TDB (on-line) 1981

Exposure Level (and Duration)	Effects	Reference
	watering, but on continued exposure sensitivity may decrease and signs and symptoms diminish	
5 ppm	Respiratory complaints, corrosion of teeth, inflammation of mucous membranes of the nose. Increased susceptibility to tuberculosis	Doc. TLV 1981
5 ppm	Men exposed in bleaching room aged prematurely; suffered from disease of the bronchi, and became predisposed to tuberculosis. Irritates skin causing sensations of burning or prickling, inflammation or even blister formation	TDB (on-line) 1981
<1 ppm (average 10.9 yr)	Male workers were exposed. No dose response relationship correlation to occurrence of colds, dyspnea, chest pain, ventilatory capacity and volumes was found. A slight excess in abnormal ECGs among exposed workers was noted. Slight correlations of exposure to anxiety, dizziness, leukocytosis, and lowered hematocrit were present. No evidence of mutagenicity or carcinogenicity was noted	Patty 1981
<1 ppm	Abnormal anterior-posterior chest films; parenchymal or hilar calcification	Chester et al. 1969. IN NIOSH 1976
0.15 ppm average (10.9 yr average)	Elevated incidence of tooth decay. No evidence of permanent lung damage. The incidence of "fatigue" was found to be greater if exposure level was in excess of 0.5 ppm. No correlation was found between the exposure level and headache, nervousness, insomnia. Moderate correlation was found between exposure level and anxiety	Patel et al. IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
	and dizziness. Some relationship was found between concentration and leukocytosis, and lowered hematocrits	
SPECIES: Rabbit		
1.7 to 0.7 ppm (up to 9 mo)	Loss of weight and an increased incidence of respiratory disease were reported	TDB (on-line) 1981
Not specified	The inhalation of small quantities of chlorine accelerated the course of experimental tuberculosis	TDB (on-line) 1981
SPECIES: Guinea Pig		
1.7 ppm (5 h/d, 87 d)	Animals given chlorine alone showed no effects. Animals exposed to tubercle bacilli alone or tubercle bacilli and chlorine showed decreased survival	Arloing et al. 1940. IN NIOSH 1976
SPECIES: Rat		
118 ppm (3 h), then 70 ppm (14 h)	Specific pathogen-free rats and diseased female rats: pre-existing lung disease increases likelihood of death from high chlorine concentration exposure ($p<0.01$). Diseased animals demonstrated increased severity of cellular response, increased proliferation of goblet cells, and aspiration of mucus. Specific pathogen-free mice showed no increase in number of polynuclear cells	Bell and Elmes 1965. IN NIOSH 1976
34 ppm (3 h/d) with daily increment increases to 170 ppm for a total duration of 60 h at 90 ppm	Specific pathogen-free and male diseased rats: pre-existing lung disease increases likelihood of death from high chlorine concentration exposure ($p <0.01$). Diseased animals demonstrated increased severity of cellular response, increased proliferation of goblet cells, aspiration of mucus. Specific pathogen-free rats showed no increase in number of polymorphonuclear cells	Bell and Elmes 1965. IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
40 ppm (3 h/d for 43 h, discrepancy not explained) at age 14 wk, then 117 ppm (3 h/d, for 29 h) at age 30 wk	14-week-old specific pathogen-free rats coughed, sneezed, huddled together. After 3 hours, noses running, sometimes blood-stained. At age 30 weeks, approximately 50% of animals died after 29 hours. Author concluded exposure to chlorine at 40 ppm did not make death from subsequently higher concentration (117 ppm) more likely	Bell and Elmes 1965. IN NIOSH 1976
1 to 3 ppm chlorine mixed with 4.5 mg/m3 mercury (5 h/d, 5 d/wk, for 3 mo)	Addition of chlorine gas to mercury vapour reduced mercury absorption	Viola and Cassano 1968. IN NIOSH 1976

7.4.2 Ingestion. No information specific to ingestion. Ingestion unlikely (Chlorine is a gas above - 34.5°C) CHRIS 1978

7.4.3 Mutagenicity and Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
Unspecified	Decrease in the ability of *Bacillus subtilis* DNA to transfer cells; increased DNA breaks	Sheh and Lederberg 1976. IN NIOSH 1976
Unspecified	No evidence of carcinogenicity	Christensen 1975. IN NIOSH 1976
SPECIES: Human		
<1 ppm (average 10.9 yr)	No evidence of carcinogenicity or mutagenicity was noted	Patty 1981

7.5 Symptoms of Exposure

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

7.5.1 Inhalation.

1. Irritation of the eyes and respiratory tract.
2. Lacrimation, conjunctivitis.
3. Sneezing, coughing, choking, sore throat, chest pain associated with coughing, huskiness or loss of voice.
4. Excessive salivation.
5. Breathing difficulties, constriction of the chest (Sax 1979).
6. Olfactory fatigue at low concentrations (Patty 1981).
7. Chronic low-level exposures may result in corrosion of the teeth, and chloracne (USDHEW 1977).
8. Chronic low-level exposure may reduce respiratory capacity (GE 1979).
9. Severely irritating at higher concentrations. Persons will remove themselves from exposure unless trapped or unconscious.
10. Headache and swelling of the accessory nasal sinuses (Braker 1977).
11. Bleeding from the nose, and sputum from larynx and trachea may be blood-tinged (Braker 1977).
12. Dizziness, restlessness, anxiety (Braker 1977).
13. Nausea, vomiting.
14. Epigastric (stomach) pain (ITII 1981).
15. Chemical tracheobronchitis.
16. Hemoptysis, cyanosis (USDHEW 1977).
17. Acute pulmonary edema, brochopneumonia.
18. Death.
19. Brief exposure to very high concentrations may cause death from suffocation.

7.5.2 Ingestion. When exposed to normal atmospheric pressures and temperatures, liquid chlorine flashes to chlorine gas. Consequently, ingestion of liquid chlorine is unlikely (AAR 1981). Contact with liquid chlorine could result in frostbite.

7.5.3 Skin Contact.

1. Local irritation, smarting.
2. Burning sensation (Lefèvre 1980).
3. Inflammation.
4. Burns (AAR 1981).
5. Painful blisters (Lefèvre 1980).

6. Shock can occur as result of pain (Lefèvre 1980).
7. Frostbite may occur when contact is made with liquid chlorine.

7.5.4 Eye Contact.

1. Stinging or burning sensation.
2. Watering eyes.
3. Conjunctivitis (Lefèvre 1980).
4. Burning sensation in the eyelids and eyes with ulceration of the tissues.
5. Local extreme irritation and or burns to the eyes (AAR 1981).
6. Opaqueness of the cornea (Lefèvre 1980).
7. Loss of sight (Lefèvre 1980).

7.6 Human Toxicity to Decay and Combustion Products

7.6.1 Hydrogen Chloride. Hydrogen chloride may form from chlorine in the presence of water vapour. Hydrogen chloride may be present as a gas or a liquid (solution in water). In contact with human skin, it causes irritation, inflammation, burns, blistering, dermatitis and profound tissue damage depending upon concentration and length of contact. In contact with eyes, it can cause stinging, burning, opaqueness of the cornea and corneal necrosis. Inhalation causes coughing, choking, ulceration of the mucosa, bronchitis, pneumonia and, in cases of exposures to extremely high concentrations, pulmonary edema and death. The TLV® is 5 ppm (8 h TWA) (Doc. TLV 1981).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Chlorine with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Heat							x							Sax 1979
Water			x				x						Forms hydrogen chloride and hypochlorous acid. Capable of explosion at certain concentrations	Sax 1979; Bretherick 1979; Cotton 1972
SPECIFIC CHEMICAL														
Acetaldehyde											x			NFPA 1978
Acetylene		x											Mixture may explode upon initiation by UV or high temp.	Bretherick 1979
Aluminum		x											Powder in gas at -20°C	Bretherick 1979
Aluminum-titanium Alloys		x											Upon heating	Bretherick 1979
Ammonia			x										When heated explodes due to formation of	Bretherick 1979

8.1 Compatibility of Chlorine 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
													nitrogen trichloride	
Antimony			x										Powdered, when spilled into gas room temperature	Bretherick at1979
Arsenic			x											Bretherick 1979
Diarsenic Disulphide			x										Powdered, when spilled into gas at room temperature	Bretherick 1979
Arsine			x										On contact at room temperature	Bretherick 1979
Barium Phosphite			x										Ignites at 90°C	NFPA 1978
Benzene							x						Explosion initiated by light	NFPA 1978
Bismuth			x										Powdered, sprinkled into dry gas. Burns spontaneously. Ignites at 80°C in liquid chlorine	Bretherick 1979
Boron			x										Burns spontaneously	Bretherick 1979
Boron Phosphide		x											Incandesces in dry gas at room temp.	Bretherick 1979
Diboron Trisulphide Brass		x												Bretherick 1979

8.1 Compatibility of Chlorine 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
Bromine Pentafluoride			x										Explodes on heating	Bretherick 1979
Calcium		x											Powder in dry gas at room temp.	Bretherick 1979
Calcium Chlorite			x											NFPA 1978
Calcium Nitride		x												Bretherick 1979
Activated Carbon		x											In contact with gas at room temp.	Bretherick 1979
Carbon disulphide			x										Liquid chlorine added to carbon disulphide in an iron cylinder results in an iron-catalyzed explosion	Bretherick 1979
Cesium		x											Reacts with luminous flame	NFPA 1978
Cesium Acetylene Carbide		x												NFPA 1978
Copper		x											Foil in dry gas at room temp.; also powder in heptane solution at <0°C	Bretherick 1979
Copper Hydride		x												NFPA 1978

8.1 Compatibility of Chlorine 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
Tricopper Diphosphide													Powdered material burns vigorously	Bretherick 1979
Cuprous Acetylide		x											Spontaneously flammable	NFPA 1978
Diborane			x											Bretherick 1979
Dibutyl Phthalate			x										At 118°C, reacts explosively with liquid chlorine	Bretherick 1979
Dichloro(methyl)-arsine													Pressure explosion due to liberation of chloromethane	Bretherick 1979
Diethyl Ether			x										Upon contact and upon exposure to light	Bretherick 1979
Diethyl Zinc		x											Spontaneously flammable	Bretherick 1979
Dioxygen Difluoride		x	x										-130 to -190°C	Bretherick 1979
Disilyl Oxide			x											Bretherick 1979
Drawing Wax			x										Reacts explosively with liquid chlorine	NFPA 1978
Ethane			x										Over activated carbon at 350°C	Bretherick 1979

8.1 Compatibility of Chlorine 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
Ethylene			x										Explosive in UV or sunlight	Bretherick 1979
Ethyleneimine			x										Forms explosive 1-chloroethyleneimine	NFPA 1978
Ethyl Phosphine			x											Bretherick 1979
Fluorine		x	x										In the presence of a spark and moisture, a violent explosion occurs	Bretherick 1979
Gasoline	x		x										When introduced into liquid chloride, starts exothermic reaction progressing to detonation	Bretherick 1979
Germanium		x											Powdered, sprinkled into dry gas	Bretherick 1979
Glycerol			x										Reacts explosively with liquid chlorine	Bretherick 1979
Hexachloro-disilane		x	x										Violent explosion may occur, vapour ignites in chlorine at 300°C	Bretherick 1979
Hydrazine		x												Bretherick 1979

8.1 Compatibility of Chlorine 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
Hydrogen			x										Exploded by almost any form of energy	Bretherick 1979
Hydroxylamine		x												Bretherick 1979
Iodine											x			NFPA 1978
Iron		x											Wire in dry gas ignites at 250°C	CM 1976; Bretherick 1979
Linseed Oil			x										Reacts explosively with liquid chlorine	NFPA 1978
Lithium		x											Reacts with luminous flame	NFPA 1978
Magnesium		x											Spontaneously flammable with moist chlorine	NFPA 1978
Manganese		x											Powder in dry gas at ambient temp.	Bretherick 1979
Trimanganese Diphosphide		x											Warm chlorine	Bretherick 1979
Mercuric Sulphide		x											At room temp.	Bretherick 1979
Mercury		x											Flame forms at 200-300°C	NFPA 1978
Trimercury Tretraphosphide		x											Ambient temperature	NFPA 1978

8.1 Compatibility of Chlorine 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
4-Morpholine-sulphenyl Chloride			x											Bretherick 1979
Nickel		x											Powdered at 600°C	Bretherick 1979
Niobium		x											Ignites when gently heated	Bretherick 1979
Nitrogen Triiodide			x											NFPA 1978
Oxomonosilane		x											The polymer of oxomonosilane ignites on contact with chlorine	NFPA 1978
Oxygen Difluoride			x										Explodes when heated	Bretherick 1979
Phenylmagnesium Bromide			x										Explosive if moisture present	Bretherick 1979
Phosphine		x											On contact at ambient temperature	Bretherick 1979
Phosphorus (white)		x	x										Explosive with liquid at -34°C, ignites on contact with gas at room temperature	Bretherick 1979
Phosphorus (red)		x											Finely divided red phosphorus ignites sponta-	Bretherick 1979

8.1 Compatibility of Chlorine 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
													neously, at 0°C, ignites in a neptane/chlorine solution	
Phosphorus Isocyanate											x			NFPA 1978
Phosphorus Oxide		x												NFPA 1978
Phosphorus Trioxide		x											Ambient temperature	Bretherick 1979
PCBs	x													NFPA 1978
Polydimethyl-siloxane			x										Reacts explosively with liquid chlorine	NFPA 1978
Polypropylene			x										Reacts explosively with liquid chlorine	NFPA 198
Potassium		x											In dry gas at ambient temp.	Bretherick 1979
Potassium Acetylene Chloride		x											Forms hydrogen chloride and carbon	NFPA 1978
Potassium Hydride		x											Burns spontaneously	NFPA 1978
Rubidium		x											Reacts with a luminous flame	NFPA 1978
Silane		x											On contact at room temp.	Bretherick 1979

8.1 Compatibility of Chlorine 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
Silicon		x											Burns spontaneously	Bretherick 1979
Silicon Hydride		x												NFPA 1978
Sodium		x											Moist gas at room temp.	NFPA 1978
Sodium Hydroxide											x		Liquid poured into 20% NaOH solution	Bretherick 1979
Stannous Fluoride		x												NFPA 1978
Steels		x											Dry steel wool ignites at 50°C, sheets at 200-250°C. Presence of soot, rust carbon or other catalyst to reduces temperature to 100°C	Bretherick 1979
Stibine			x										Gaseous, also with chlorine water	Bretherick 1979
Strontium Phosphide		x												NFPA 1978
Sulfamic Acid			x								x		Forms nitrogen trichloride	NFPA 1978
Tellurium	x												Incandesces in gas when warmed slightly	Bretherick 1979

8.1 Compatibility of Chlorine 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
Tetramethyl Diarsine		x											Spontaneously flammable	NFPA 1978
Tetraselenium Tetranitride			x										On contact	Bretherick 1979
Thorium	x	x											In dry gas upon warming	Bretherick 1979
Tin	x	x											Ignites in liquid chlorine at -34°C, in dry gas upon warming	Bretherick 1979
Titanium		x											Ignition may occur on contact with dry gas or liquid. Moisture will prevent ignition	Bretherick 1979
Tungsten Dioxide	x												Incandesces on warming	Bretherick 1979
Turpentine			x											NFPA 1978
Uranium		x											Ignites spontaneously at 150°C in dry gas	Bretherick 1979
Vanadium			x										Powder on contact at 0°C with pressurized liquid	Bretherick 1979
Zinc		x											In moist gas at room temperature	Bretherick 1979

8.1 Compatibility of Chlorine 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
<u>CHEMICAL GROUPS</u>														
Alcohols			x			x							Produces unstable alkyl hypochlorites which decompose in the cold and explode on exposure to sunlight or heat	Bretherick 1979
Alkylisothiourea Salts			x										Explosion on long contact or with excess chlorine	NFPA 1978
Alkylphosphines						x					x		Mono or dialkyl compounds	NFPA 1978
Hydrides		x											K, Na and Cu at ambient temperature	Bretherick 1979
Saturated Aliphatic Hydrocarbons											x			Bretherick 1979
Silicones			x										Explosive on heating	Bretherick 1979
Strong Reducing Agents			x											EPA 600/2-80-076
Sulphides		x												Bretherick 1979
Trialkylboranes		x												Bretherick 1979

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

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

9.1.1 Fire Concerns. Chlorine is nonflammable and nonexplosive in both gaseous and liquid states (HCG 1981). Contact with combustible substances (such as gasoline and petroleum products, turpentine, alcohols, acetylene, hydrogen, ammonia and sulphur) and finely divided metals may cause fires and explosions (NIOSH/OSHA 1981; NFPA 1978). In the presence of water or moisture, chlorine will undergo hydrolysis and form corrosive HCl which can attack metals, liberating hydrogen which in turn can combine explosively with chlorine (Hooker MSDS 1977). Chlorine will support the burning of most combustible material, just as oxygen does. Flammable gases and vapours can form explosive mixtures with chlorine. Intense local heat (above 215°C) on steel walls can cause the steel to ignite in chlorine (GE 1979). Elevated temperatures may also cause cylinders to burst (NIOSH/OSHA 1981). Fusible plugs will melt first, causing release of pressure, but intense heat may still cause cylinders to rupture.

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to help prevent rupture and to reduce vapours (ERG 1980). Water spray may also be used to direct escaping gas away from men effecting the shut-off (NFPA 1978). Do not apply water directly to the leak or inside containers (EAG 1978).

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

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

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

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

Approximate Size of Spill	Distance to Evacuate from Immediate Danger Area	For Maximum Safety, Downwind Evacuation Area Should Be
20 m^2	145 m (192 paces)	1,620 m long, 810 m wide
35 m^2	220 m (288 paces)	2,430 m long, 1,620 m wide
55 m^2	275 m (360 paces)	2,430 m long, 1,620 m wide
75 m^2	310 m (408 paces)	3,240 m long, 2,430 m wide

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

9.1.4 Spill Actions.

9.1.4.1 General. Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area (MCA 1970). If a chlorine leak develops in transit through a populated area, keep the vehicle or tank car moving until open country is reached in order to minimize the hazards of escaping gas. If possible, turn the container to a position such that gas instead of liquid escapes (HCG 1981). Leaks around valve stems can usually be stopped by tightening the packing nut or gland. If confronted with a container leak other than at the valves, chlorine emergency kits (if available) may be used to stop the leak (HCG 1981). If it is not possible to stop the leak, the gaseous chlorine should be directed into an alkaline solution. "Never immerse the container" but pass the chlorine into the solution through an iron pipe or weighted rubber hose (NSC 1979). Naturally, the connections will not be gas tight but should be rigged in such a manner that most of the gas will be directed to the neutralizing solution. Chlorine may be absorbed in solutions of caustic soda (sodium hydroxide) or soda ash (sodium carbonate), or in agitated hydrated lime (calcium hydroxide) slurries. Caustic soda is recommended as it absorbs chlorine most readily. The following are recommended proportions of alkali and water needed to absorb different quantities of chlorine (HCG 1981):

Chlorine Container Capacity (kg)	Caustic Soda		Soda Ash		Hydrated Lime*	
	NaOH (kg)	Water (L)	Na_2CO_3 (kg)	Water (L)	$Ca(OH)_2$ (kg)	Water (L)
45	57	151	136	379	57	473
68	85	227	204	568	85	712
908	1,135	3,028	2,724	7,570	1,135	9,463

* Hydrated lime solution must be continuously and vigorously agitated while chlorine is being absorbed (HCG 1981).

Chlorine gas may also be absorbed through solutions containing reducing agents such as sodium bisulphide and sodium bicarbonate (NIOSH/OSHA 1981).

Urethane foam has been recommended to control chlorine spills (EPA R2-73-185).

9.1.4.2 Spills on land. Any spill of liquified chlorine or chlorine-contaminated water should be contained, if possible, by forming mechanical or chemical barriers to prevent spreading. Fly ash or cement powder may be applied to absorb chlorine-contaminated water (EPA 670/2-75-042). Recover any liquid if possible (Dow ERIS 1981).

The following treating materials may be considered to either neutralize or immobilize chlorine spills:

- Neutralizing agents (CG-D-38-76): calcium carbonate, hydroxide or oxide, adventitious crustacean shells, sodium hydroxide or carbonate, limestone or dolomite.
- Reducing agents (CG-D-38-76): calcium sulphite hemihydrate, lignite filtrate or cellulose sulphite liquor from wood pulping.
- Sorbents (for chlorine-contaminated water) (CG-D-38-76): activated carbon, polyurethane, polyolefin and Dowex 1.
- Sodium thiosulphate may also be used for dechlorination (OHM-TADS 1981).

9.1.5 Cleanup and Treatment.

9.1.5.1 Spills in water. If chlorine has solubilized in the water, application of activated carbon at 10% the spill amount over the region occupied by 10 mg/L or greater concentration is recommended. Mechanical dredges or lifts may be used to remove the immobilized masses of pollutants and precipitates (EPA 670/2-75-042).

9.1.5.2 General. For treatment of contaminated water the following procedure is recommended (EPA 600/2-77-227): gravity separation of solids followed by acidification, using sulphuric acid, to pH 2.0 to 3.0. Sodium bisulphite is added, as a reducing agent, until little or no residual chlorine is attained. The solution is then neutralized to pH 7.0 using either an acid (e.g., HCl) or a base (e.g., Na_2CO_3). Carbon adsorption is recommended to remove low concentrations of chlorine.

9.1.6 Disposal. Waste chlorine and chlorine-contaminated water must never be discharged directly into sewers or surface waters. Following treatment either at the spill site or at a waste management facility, the resultant sludge can be disposed of to a secure landfill. If hypochlorite is produced during treatment, it can be destroyed by adding sodium sulphite or by decomposing the basic solution at 50 to 70°C in the presence of copper or iron catalysts. It should be noted that the decomposition may double for each 6°C increase in temperature above room temperature. The following reaction applies: $2NaOCl \xrightarrow{\text{catalyst}} 2\ NaCl + O_2$ (Hooker PIM 1979; CE 1981).

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 must be worn.

If the spilled material is known to be chlorine:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate clothing necessary to prevent any possibility of skin contact with liquid chlorine, and to prevent the skin from becoming frozen with vessels containing liquid chlorine (NIOSH/OSHA 1981).
- Splash-proof safety goggles should be worn where there is any possibility of liquid chlorine contacting the eyes (NIOSH/OSHA 1981). Chemical safety goggles are also recommended (GE 1979).
- PVA is recommended for gloves (Ashland MSDS 1978).
- Cloropel has been recommended as a chemical suit material (good resistance) for protection against chlorine (EE-20).
- Non-impervious clothing which becomes contaminated with chlorine should be removed immediately and not reworn until the chlorine is removed from the clothing (NIOSH/OSHA 1981).
- Eye wash stations and chemical safety showers should be readily available to areas of use and potential spill situations (GE 1979).

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

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Gas concentration 25 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against chlorine.
	A gas mask with a chin-style or a front- or back-mounted canister providing protection against chlorine.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
Greater than 25 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any full-facepiece gas mask providing protection against chlorine.
	Any escape self-contained breathing apparatus with a full facepiece.

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

** Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of chlorine; 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 25 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

9.1.8 **Special Precautions.** Store chlorine containers in well-ventilated areas of low fire potential, away from sources of heat and ignition (GE 1979). Protect against physical damage. Separate from combustible, organic or easily oxidizable materials and especially isolate from acetylene, ammonia, hydrogen, hydrocarbons, ether, turpentine and finely divided metals (NFPA 1978).

9.2 Specialized Countermeasures Equipment, Materials or Systems

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

Leak Plugging	Chlorine Institute Emergency Kit "A", Kit "B", and Kit "C"
Land Containment	Portafoam

10 PREVIOUS SPILL EXPERIENCE

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

10.1 Tank Car Leak (Personal Communication with EEB 1982)

In a railroad incident in the Southern United States, a chlorine tank car ruptured and leaked gas. The leak could not be stopped; the response crew conceived of a plan to dump and neutralize the contents. To this end, the ditch of the right-of-way was diked and lined with a polymeric membrane to form a reservoir for the chlorine remaining in the tank car. The pit was loaded with sufficient sodium hydroxide pellets to neutralize the chlorine. The manway of the tank was loosened so that the chlorine would pour out when the car was inverted. The car was then overturned and the liquid chlorine rushed out into the neutralization pit, but continued on over the bank and the last remaining liquid disappeared from view in a short time. There was little evidence of contact or reaction with the sodium hydroxide. Chlorine fumes covered the area behind the path of the rapidly departed liquid, compounding the immediate hazard.

This experience illustrates that liquid chlorine can exhibit behaviour similar to cryogens. The chlorine was spilled into the pit with sufficient velocity to continue out of the ditch and into the adjoining field. This apparently frictionless movement was caused by trapped gas under the liquid. The liquid initially is evaporated rapidly by contact with the warm surface (e.g., land) and the gas is temporarily trapped under the surface of the liquid and thus presents very little friction to the overriding liquid mass. The countermeasure proposed in this situation would have worked if either the horizontal velocity of the chlorine liquid had been very low (obviously very difficult to do) or if the chlorine had been added slowly enough to react and/or evaporate before leaving the pit area. In the latter case, it would have been more appropriate to use a caustic solution and discharge the liquified chlorine into this, so that the resulting vapours would dissolve in the aqueous solution and thus not escape to the air.

10.2 Chlorine Ton Container Leak (Personal Communication with EPS 1983)

On September 25, 1978, a shipment of 12 "ton" containers (or Tonners) of chlorine was being transported by truck through the Vancouver area to the dock area. Six of the containers broke loose when the truck braked at a downtown intersection. The containers fell onto the street and at least one was struck by a passing motorist. Another of the ton containers developed a leak at the welded seam and liquid chlorine began to escape. Fire and police sealed off the area, began evacuation and called an industry emergency response team. The fire department used fog over the cylinder in an attempt to knock down the chlorine vapours but were advised very shortly after to stop as the leak could be increased by the corrosive solution (water and chlorine producing hydrochloric acid). By this time the chlorine had affected a number of people - police, fire fighters and civilians. It was necessary to bring in additional breathing apparatus for the police from a military base.

The industry team arrived about 1 1/2 hours later with a "chlorine emergency kit". The kit could not be used to seal off a leak at the welded seam; it is designed to seal off a leaking end or bonnet and leaks in the cylindrical portion of a ton container. The wind shifted and additional people had to be evacuated. Two hours after the start of the incident, a tarpaulin was placed over the leaking chlorine container and water fog applied over the top. This action reduced the vapour emission substantially. Three hours after the onset, a truck with caustic soda (sodium hydroxide) arrived and the chlorine was neutralized by piping it into this solution. It was estimated that one-third of the chlorine was still in the tank before neutralization. The leaking container and the others were removed from the scene. Four to five hours after the incident began, the area was cleaned and residents could move back in. Seventy-seven persons were admitted to hospital; 37 were fire or police personnel and 40 were civilians.

A number of points can be raised from this incident:

1. Existing patch kits are not capable of sealing leaks at the weld seam of the ton container.
2. Chlorine emission could have been reduced by turning the ton container so that the leak was at its top, thereby emitting the gas instead of the liquified chlorine.
3. Firemen misunderstood the notion of fogging to knock down vapours. This should have been done by spraying water with fog nozzles onto the vapour (which was done) but away from the container. If sprayed onto the container, the corrosive mixture of chlorine in water (producing hydrochloric acid) could have enlarged the leak.

4. The use of a tarpaulin over the leaking container along with the water fog application appears to be an effective temporary measure for suppressing vapours.
5. Neutralization of the remaining contents could have been attempted much earlier, thus reducing the vapour emission time.

11 ANALYTICAL METHODS

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

Methods have been documented here for analyses 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 Chlorine in Air

11.1.1 Colourimetric (NIOSH 1977; APHA 1977). A range of 0.05 to 1.0 ppm free chlorine can be measured in a 30 L air sample. This range may be extended by varying the sample volume.

A measured volume of air is drawn through a fritted bubbler containing 100 mL of dilute methyl orange. This absorbing solution is prepared by diluting 100 mL of a 0.05 percent stock solution to 1 L. The sampling rate should be between 1 and 2 L/min. A suitable spectrophotometer set at a wavelength of 505 nm is used to determine the extent of bleaching of the methyl orange. Depending on the concentration of chlorine, cells ranging in size from 1 to 5 cm may be used. Since the sampled solutions are light-sensitive, they must be protected from light. Sources of interference are free bromine, sulphur dioxide, nitrogen dioxide and ozone. This is a reliable method with an average analytical error of less than ± 5 percent.

11.2 Qualitative Method for the Detection of Chlorine in Air

Starch-iodide papers are used to indicate the presence of chlorine at concentrations as low as 2 to 6 ppm. Chlorine reacts with potassium iodide to release free iodine which then reacts with the starch to produce a blue colour. The sensitivity can be increased to 0.25 to 12 ppm by using starch-iodide paper also coated with glycerin and sulphurous acid (Sittig 1974).

11.3 Quantitative Methods for the Detection of Chlorine in Water

Elemental chlorine in water initially undergoes hydrolysis to form free available chlorine. This consists of aqueous molecular chlorine, hypochlorous acid and hypochlorite ion. Free chlorine combines readily with ammonia nitrogen and nitrogenous compounds to form combined available chlorine. Residual chlorine is the available chlorine present in water after the addition of chlorine. The following methods determine the above forms of chlorine but not chlorine present as chloride.

11.3.1 Iodometric Titration (AWWA 1976). The minimum detectable concentration is approximately 40 µg/L (0.04 ppm) chlorine in water if 0.01 N sodium thiosulphate is used with a 500 mL sample.

A sample size that will require no more than 20 mL of 0.01N sodium thiosulphate to complete the titration is recommended. Acetic acid is added to reduce the pH to between 3.0 and 4.0. About 1 g of potassium iodide is added. The titration is performed using 0.025 N or 0.01 N sodium thiosulphate with a starch indicator. A blank titration must be done. Turbidity of the sample will obscure the end point. Organic matter, manganic manganese and chromates interfere with this method. The iodometric method is considered to be the standard method.

11.3.2 Starch-iodide Titration (ASTM 1979; AWWA 1976). Concentrations of chlorine as low as 1 mg/L (1 ppm) may be determined using a 1,000 mL sample.

The sample is added to 5 mL of 0.00564 N sodium thiosulphate or 0.00564 N phenylarsine oxide solution and 1 g of potassium iodide. The pH is adjusted to 4.0 with acetate buffer. The solution is titrated with 0.0282 N biiodate solution using starch indicator. This method is used only for total residual chlorine. Although excessive turbidity and colour obscure the end point, this method may be used for water that contains appreciable amounts of organic matter.

11.3.3 Amperometric Titration (ASTM 1979; AWWA 1976). A range of 0 to 2.0 ppm chlorine can be determined in a 100 mL sample. When higher concentrations of chlorine are present, the sample may be diluted.

A sample size that will require 2 mL of titrant is recommended. Potassium iodide is added to 200 mL of sample followed immediately by acetate buffer solution of pH 4.0. The sample is titrated with 0.00564 N phenylarsine oxide solution using a suitable potentiometer. Care must be taken that chlorine is not volatilized and lost during stirring. This method is applicable to all types of water but requires greater technical skill than methods which have a coloured end point.

11.4 Qualitative Method for the Detection of Chlorine in Water

Starch-iodide papers are used to indicate the presence of chlorine at concentrations as low as 2 to 6 ppm. Chlorine reacts with potassium iodide to release free iodine which then reacts with the starch to produce a blue colour. The sensitivity can be increased to 0.25 to 12 ppm by using starch-iodide paper also coated with glycerin and sulphurous acid (Sittig 1974).

11.5 Quantitative Methods for the Detection of Chlorine in Soil

11.5.1 Silver Nitrate Titration (Bear 1964). Concentrations of more than 1 mg/L chlorine in the extract solution may be measured.

A sample of approximately 2 g of finely ground soil, accurately weighed, is collected. It is fused with sodium carbonate and sodium nitrate in an electric furnace using a platinum crucible. The fused mass is taken up in water, digested and filtered. A suitable aliquot is pH adjusted to about 4.0 with sulphuric acid and then diluted. The solution is titrated with 0.1 N standard silver nitrate solution using potassium chromate as the indicator. The method is suitable for determining large amounts of chlorine. An electric furnace must be used since there will be sulphuric contamination from the flame of a non-electric furnace and this interferes with the analysis. The method is accurate but is time-consuming.

11.5.2 Iodometric Titration (Hesse 1972). Concentrations as low as 1 mg/L (1 ppm) in the titrated solution may be determined.

A representative soil sample is fused with very pure sodium carbonate. A platinum crucible and an electric furnace must be used. The chlorine in the melt is oxidized to elemental chlorine with potassium permanganate and absorbed in potassium iodide solution. The liberated iodide is titrated with 0.1 N sodium thiosulphate using a starch indicator. A blank determination is essential. If bromine is present, it is determined along with chlorine, so it must be determined separately and subtracted. Iodine also interferes but is not usually present in soil in large amounts.

11.6 Qualitative Method for the Detection of Chlorine in Soil

Starch-iodide papers are used to indicate the presence of chlorine at concentrations as low as 2 to 6 ppm. Chlorine reacts with potassium iodide to release free iodine which then reacts with the starch to produce a blue colour. The sensitivity can be increased to 0.25 to 12 ppm by using starch-iodide paper also coated with glycerin and sulphurous acid (Sittig 1974).

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EnviroTIPS

Common Abbreviations

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

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