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Information for

Problem

Spills

SODIUM HYPOCHLORITE

March 1985

Canadä

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

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

EnviroTIPS manuals are available from

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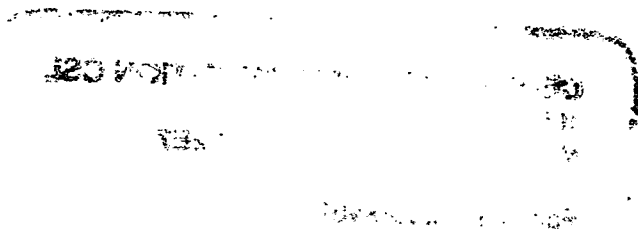Environment Canada
Ottawa, Ontario
CANADA
K1A 1C8

SODIUM HYPOCHLORITE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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

March 1985

FOREWORD

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

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1   SUMMARY

SODIUM HYPOCHLORITE (NaOCl)

Green to yellow watery liquid with a chlorine-type (bleach) odour

SYNONYMS

Chlorox, Dakins Solution, Chloros, Antiformin, B-K Liquid, Carrel-Dakin Solution, Hychlorite, Liquid Bleach, Javel Water

IDENTIFICATION NUMBERS

UN. No. 1791 (>5 percent solutions); CAS No. 7681-52-9; OHM-TADS No. 7800016; STCC No. 7944123 (<7 percent solution), 4932378 (>7 percent solution)

GRADES & PURITIES

Aqueous solutions, 5-15 percent
Household, 5-5.5 percent
Commercial, 9-15 percent

IMMEDIATE CONCERNS

Fire: Not combustible

Human Health: Toxic by inhalation and ingestion

Environment: Harmful to aquatic life at low concentrations

PHYSICAL PROPERTY DATA

Shipping state: liquid (aqueous solution)
Boiling Point: decomposes before boiling
Melting Point: decomposes (40°C)
Flammability: not combustible

Specific Gravity: 1.21 (14 percent aqueous solution, 20°C)
Solubility (in water): 29.4 g/100 g (0°C)
Behaviour (in water): sinks and mixes

ENVIRONMENTAL CONCERNS

Sodium hypochlorite is toxic to aquatic life at low concentrations, generally below 10 mg/L. It is also toxic to land animals by ingestion. It is not persistent in the environment and has no potential for bioaccumulation or food chain contamination.

HUMAN HEALTH

No TLV® or IDLH established

Exposure Effects

Inhalation: Inhalation of free chlorine produces irritation of nose and throat and coughing, corrosive to tissue, may cause pulmonary edema or shock

Contact: Irritation, blistering and possibly eczema will occur

Ingestion: Inflammation of mouth, pharynx, esophagus and stomach, erosion of mucous membranes, hemorrhage and possibly coma may occur

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE". Notify manufacturer. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not flammable or combustible. Use foam, dry chemical, carbon dioxide, water spray or fog to extinguish fires where sodium hypochlorite is involved. Cool fire-exposed containers with water.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill or divert to impermeable holding area. Remove material with pumps or vacuum equipment. Absorb small amounts of spill with natural or synthetic sorbents and shovel into containers

Water: Contain by damming, water diversion or natural barriers

2   PHYSICAL AND CHEMICAL DATA

Physical State Properties Note: Throughout this manual, the solutions will be discussed except where specifically noted. Solid sodium hypochlorite does not exist under normal circumstances

Appearance	Greenish yellow liquid (Olin MSDS 1980)
Usual shipping state	Liquid: 5-15 percent aqueous solution (Kirk-Othmer 1978)
Physical state at 15°C, 1 atm	Unstable solid. Sodium hypochlorite only exists as an aqueous solution at room temperature. One hydrate ($NaOCl \cdot 5H_2O$) is somewhat stable (Kirk-Othmer 1978)
Melting point	Decomposes above 40°C; $NaOCl \cdot 5H_2O$ melts at 18°C (Kirk-Othmer 1978)
Boiling point	Decomposes above 40°C before boiling (Olin MSDS 1980)

Densities

Specific gravity	1.21 (14 percent aqueous solution) (CCPA 1984) 1.12 (9-13 percent aqueous solution) (Olin MSDS 1980)

Fire Properties

Flammability	Not combustible (Olin MSDS 1980)
Decomposition temperature	>40°C (Kirk-Othmer 1978)

Other Properties

Molecular weight of pure solid	74.44 (CRC 1980)
Constituent components of typical commercial grade	5-15 percent sodium hypochlorite, 95-85 percent water 0.25-0.35 percent free alkali, 0.50-1.50 percent NaCl (Kirk-Othmer 1978; Ullmann 1975)
Heat of formation	-346.0 kJ/mole (25°C) (Crystal) (Lange's Handbook 1979; Kirk-Othmer 1978) -304.0 kJ/mole (25°C) (Aqueous) (Kirk-Othmer 1978)
Heat of solution	-15 kJ/mole (est.) (20°C) (CHRIS 1978)

Solubility

In water   29.4 g/100 g (0°C), 53 g/100 g (25°C),
110 g/100 g (40°C) (Lange's Handbook 1979)
29.3 g/100 g (25°C) (pentahydrate,
$NaOCl \cdot 5H_2O$) (OHM-TADS 1981)

SODIUM HYPOCHLORITE

CONVERSION NOMOGRAMS

Temperature

°C -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100

°F -40   0   50   100   150   200

Pressure 1 kPa = 1 000 Pa

kPa 0 10 20 30 40 50 60 70 80 90 100

Atmospheres 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

kPa 0 10 20 30 40 50 60 70 80 90 100

psi 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

kPa 0 10 20 30 40 50 60 70 80 90 100

mmHg(torr) 0 100 200 300 400 500 600 700 800
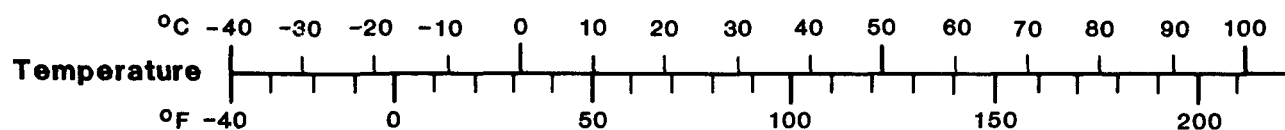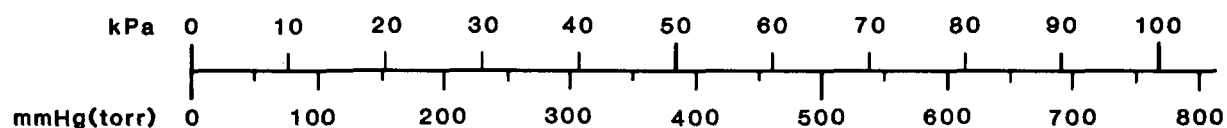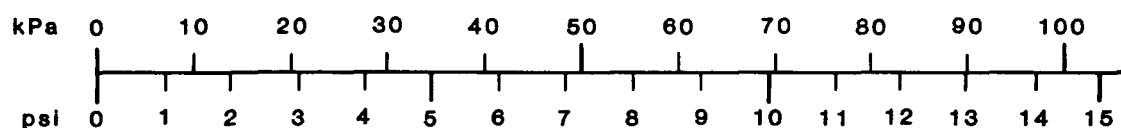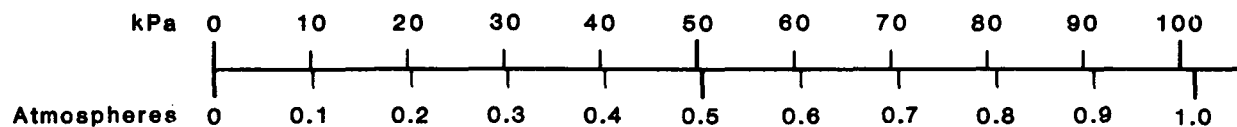
Viscosity

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

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

Concentration (in water)
1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J

kJ 0 10 20 30 40 50 60 70 80 90 100

kcal 0   5   10   15   20   25

kJ 0 10 20 30 40 50 60 70 80 90 100

BTU 0 10 20 30 40 50 60 70 80 90 100

kg/m³ 0 10 20 30 40 50 60 70 80 90 100

Density

lb/ft³ 0   1   2   3   4   5   6
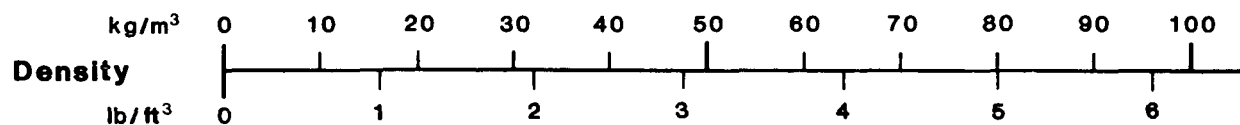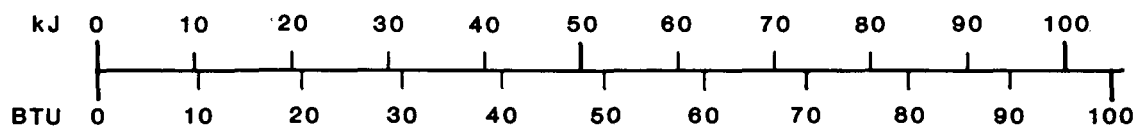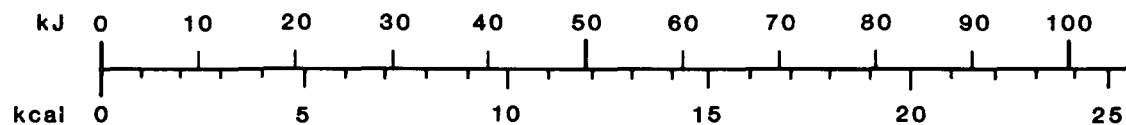
3   COMMERCE AND PRODUCTION

3.1   Grades, Purities (Olin MSDS 1980; Kirk-Othmer 1978; Ullmann 1975; Sauter 1982; WPC 1977)

Sodium hypochlorite is sold as solutions generally in the range of 5 to 15 percent free chlorine content by weight.   The free chlorine content roughly corresponds to the weight percent sodium hypochlorite content and thus these are often used interchangeably.   The most commonly sold solution for industrial chlorination is 12 percent free chlorine, which corresponds to 10.8 percent alkaline sodium hypochlorite content.   Household solutions are typically 5-5.5 percent free chlorine; commercial solutions are usually 9-15 percent.

Sodium hydroxide is often added to stabilize the sodium hypochlorite solutions. A 15 percent free chlorine (wt. percent) solution has a half-life of about 100 days without alkali such as sodium hydroxide; with 0.25-0.35 percent free alkali, this life is extended by several multiples.   Solutions above 35 percent free chlorine are not stable.   In addition to sodium hydroxide, sodium hypochlorite solutions often contain sodium chloride (salt) which is a degradation product as well as an impurity from production.   Sodium chloride contents generally range from 0.5 to 1.5 percent (w/w).

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

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

Bristol-Myers Canada Ltd.
Bristol-Myers Products Canada Division
99 Vanderhoof Avenue
Toronto, Ontario
M4G 2H6
(416) 421-6000

Chlorox Co. of Canada Ltd.
901-112 West Pender Street
Vancouver, British Columbia
V6E 2S1
(604) 684-6511

Canadian Miraclean Products Ltd.
2531 No. 5 Road
Richmond, British Columbia
V6X 2S8
(604) 278-8441

C-I-L Inc.
90 Sheppard Avenue East
North York, Ontario
M2N 6H2
(416) 226-6110

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

Diversey Corporation of Canada
201 City Centre Drive
Mississauga, Ontario
L5B 2T4
(416) 273-4690

Lavo Limited
1880 rue de Chambly
Montreal, Quebec
H1W 3J2
(514) 526-7783

Stanchem, Industrial Chemical Division
PPG Industries Canada Ltd.
50 St. Clair Avenue
Toronto, Ontario
M4V 1M9
(416) 923-5441

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

Welland Chemical Ltd.
3068 Universal Drive
Mississauga, Ontario
L4X 2C8
(416) 625-5690

3.3 Other Suppliers (CBG 1980; CCPA 1983; Corpus 1983)

Bayer (Canada) Inc.
7600 TransCanada Highway
Pointe Claire, Quebec
H9R 1C8
(514) 697-5550

Shefford Chemicals Ltd.
1028 Principale
Granby, Quebec
J2G 8C8
(514) 378-0125

Chlorox Canada
317 Orenda Drive
Brampton, Ontario
L6T 1G4
(416) 457-1922

Stanchem, Industrial Chemicals Division
PPG Industries Canada Ltd.
Beauharnois, Quebec
J6N 3C3
(514) 429-4641

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

3.4 Major Transportation Routes (Corpus 1983)

Current Canadian production of sodium hypochlorite is very widespread, occurring in eight provinces. The largest production facilities are in Montreal and Bécancour, Quebec, in Toronto, Ontario, and in Moncton, New Brunswick. Transportation is relatively universal.

3.5 Production Levels (Corpus 1983)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Merchant Manufacture	
Bristol-Myers Canada, Moncton, N.B.	2.5
Bristol-Myers Canada, Quebec City, Que.	1

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Merchant Manufacture (Cont'd)	
Bristol-Myers Canada, Montreal, Que.	4
Bristol-Myers Canada, Toronto, Ont.	5
Bristol-Myers Canada, Winnipeg, Man.	2
Bristol-Myers Canada, Edmonton, Alta.	2
Bristol-Myers Canada, Vancouver, B.C.	2
C-I-L Inc., Bécancour, Que.	2.5
C-I-L Inc., Cornwall, Ont.	4
Canadian Miraclean Products, Vancouver, B.C.	1.5
Canso Chemicals, Abercrombie Pt., N.S.	1
Diversy (Canada), Mississauga, Ont.	1.5
Lavo, Montreal, Que.	1
Old Dutch Chemicals, Weston, Ont.	1
Saskatoon Chemical, Saskatoon, Sask.	1
Stanchem (PPG), Beauharnois, Que.	1
Welland Chemical, Sarnia, Ont.	1
TOTAL	34.00
Captive Production	
Abitibi Paper, Smooth Rock Falls, Ont.	3
B.C. Forest Products, Crofton, B.C.	5
Boise Cascade Canada, Newcastle, N.B.	7
Boise Cascade Canada, Fort Frances, Ont.	4
Canadian International Paper, La Tuque, Ont.	2
Cariboo Pulp & Paper, Quesnel, B.C.	6.8
Consolidated-Bathurst, Portage du Fort, Que.	5
Consolidated-Bathurst, Trois-Rivières, Que.	3
Crown Zellerbach Canada, Campbell River, B.C.	8
Eddy Forest Products, Espanola, Ont.	5
Fraser, Atholville, N.B.	3
Fraser, Edmundston, N.B.	4
Great Lakes Forest Industries, Thunder Bay, Ont.	5
Intercontinental Pulp, Prince George, B.C.	4
James River-Marathon, Marathon, Ont.	5
Kimberley-Clark of Canada, Terrace Bay, Ont.	5
MacMillan Bloedel, Nanaimo, B.C.	15
MacMillan Bloedel, Port Alberni, B.C.	4
MacMillan Bloedel, Powell River, B.C.	4
Procter & Gamble Cellulose, Grande Prairie, Alta.	7
Prince Albert Pulp, Prince Albert, Sask.	7.5
St. Regis Alberta, Hinton, Alta.	5
Tahsis, Gold River, B.C.	6.5
Tembec Industries, Temiskaming, Que.	4
Western Forest Products, Port Alice, B.C.	4

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Captive Production (Cont'd)	
Western Forest Products, Wood Fibre, B.C.	5
Weyerhaeuser Canada, Kamloops, B.C.	4
TOTAL	140.8
TOTAL NAMEPLATE CAPACITY	174.8
Domestic Production (1982)	153
Imports (1982)	0.1
TOTAL SUPPLY	153.1

3.6   Manufacture of Sodium Hypochlorite (Shreve 1977)

3.6.1   Manufacturing Process. The most common method for manufacturing sodium hypochlorite is absorption of gaseous chlorine in aqueous sodium hydroxide:

$$Cl_2 + 2NaOH \rightarrow NaCl + H_2O + NaOCl$$
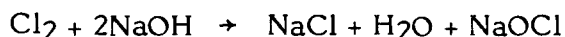
Concentrations under 15 percent are generally produced.

3.7   Major Uses in Canada (Corpus 1983)

Sodium hypochlorite is used in wood pulp bleaching, laundry bleach, effluent treatment, textile bleaching, sanitation (industrial, swimming pool) and food processing plants (odour control and sanitation). In 1982, 85 percent of domestic production was used for wood pulp bleaching and 10 percent was used for laundry bleach.

3.8   Major Buyers in Canada (Corpus 1983)

Burns Bros, Calgary, Alta.
Canada Packers, Toronto, Ont.
Canadian Int'l Paper, Gatineau, Que.
Dominion Cellulose, Toronto, Ont.
Dominion Electroplating, Midland, Ont.
Domtar, Cornwall, Ont.; Beauharnois, Que.
Englehard Industries, Toronto, Ont.
Goodyear Canada, Toronto, Ont.
Gulf & Western (Canada), Windsor, Ont.
Houdaille Oshawa, Oshawa, Ont.
Kert Chemical, Toronto, Ont.
Nacan Products, Collingwood, Ont.
Orangeville Municipality, Orangeville, Ont.
Polysar, Sarnia, Ont.
Prentice Chemical, Hamilton, Ont.

St. Lawrence Starch, Mississauga, Ont.
St. Lawrence Textiles, Hawkesbury, Ont.
Savage Products, Calgary, Alta.
Shefford Chemicals, Granby, Que.
Swift Canadian, Toronto, Ont.

4   MATERIAL HANDLING AND COMPATIBILITY

4.1   Containers and Transportation Vessels

4.1.1   Bulk Shipment. Sodium hypochlorite solutions are shipped bulk in specially designed railway tank cars and tank motor vehicles. In Canada, most bulk shipments are by truck.

4.1.1.1   Railway tank cars. Railway tank cars used in the transportation of sodium hypochlorite solutions are not specifically regulated. Table 2 lists some cars typically used. Figure 1 shows a 111A100W2 railway car. Table 3 provides railway tank car details associated with this drawing. Sodium hypochlorite cars are usually unloaded from the top using compressed air (PC 1982). The liquid is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with a 51 mm (2 in.) unloading connection valve. Air pressure of 207 kPa (30 psi) is applied through the 25 mm (1 in.) air connection valve.

A safety relief valve set at 518 kPa (75 psi) or a safety vent set at 690 kPa (100 psi) is required on top of the rail car. A gauging device, either the rod type or the tape type, is required. The maximum pressure allowable for the 111A100W2 rail cars is 448 kPa (65 psi). When the 111A60W2 cars are used, this maximum pressure would be 276 kPa (40 psi) (TCM 1979). Both these pressures exceed the maximum compressed air pressure of 207 kPa (30 psi) used during unloading. Sodium hypochlorite is never transported under pressure (PC 1982).

4.1.1.2   Tank motor vehicles. The most common means of bulk transport is by tank truck. Capacities vary from 2300 to 20 000 L (500-4500 gal.) (Sauter 1982). Highway tankers transporting sodium hypochlorite solutions are unloaded from the top, usually with the stand pipe extended down over the back of the tank. Compressed air is used for unloading. The air inlet is usually a 25 mm (1 in.) diameter male threaded connection located at the top of the trailer through which air pressure not exceeding 207 kPa (30 psi) may be applied (PC 1982).

Shipments by highway tanker are not subject to any specific requirements of the Transportation of Dangerous Goods Code (TDGC 1980).

4.1.2   Packaging. In addition to bulk shipments, sodium hypochlorite solutions are also transported in drums. Drums fabricated from a variety of construction materials are permitted. Table 4 lists drum types and descriptions (TDGC 1980). Steel drums are lined with materials such as polyethylene or PVC.

TABLE 2   RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
111A60W2	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi). Top unloading arrangement required. Bottom outlet prohibited; bottom washout optional. Test pressure 414 kPa (60 psi). Interior lined.
111A100W2	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Safety valve (518 kPa) (75 psi) or safety vent (690 kPa) (100 psi). Top unloading arrangement required. Bottom outlet prohibited; bottom washout optional. Test pressure 690 kPa (100 psi). Interior lined.
111A60W5	Steel fusion-welded tank without dome. Uninsulated or insulated. Rubber-lined tank. 2% minimum outage. Gauging device. Safety vent (242 kPa) (35 psi). Top unloading arrangement required. Bottom outlet or washout prohibited. Test pressure 414 kPa (60 psi).

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

FIGURE 1

SODIUM HYPOCHLORITE SOLUTIONS | RAILWAY TANK CAR - CLASS 111A100W2

(Reference - TCM 1979, AAR 1982, RTDCR 1974)

MANWAY WITH 203 mm (8 in) I.D. FILL HOLE

25.4 mm (1 in) AIR CONNECTION AND VALVE

50.8 mm (2 in) DISCHARGE OUTLET

1.8 m (6 ft)

n.t.s.
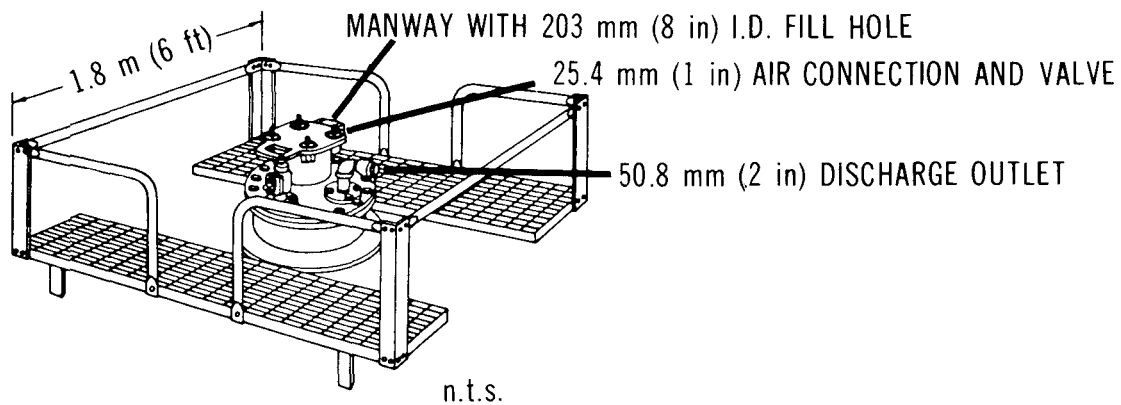
Detail of loading platform

LOADING PLATFORM

SAFETY VENT OR SAFETY VALVE

DRIP LEDGE

WASHOUT

13.6 m (44 ft 7¼ in) COUPLED LENGTH
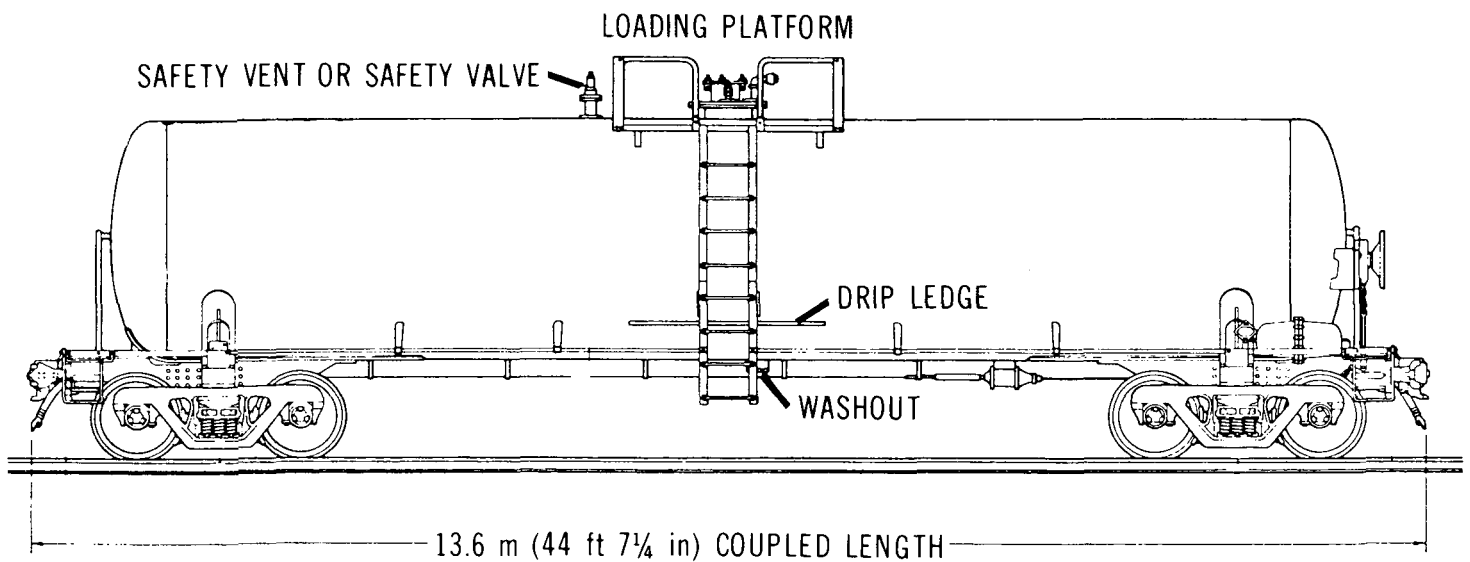
Approximate Scale 1 : 72

Illustration of train car layout

TABLE 3   RAILWAY TANK CAR DETAILS - CLASS 111A100W2
(TCM 1979; AAR 1982; RTDCR 1974)

Description	Dimension	Notes
Overall		
Nominal capacity	50 500 L (11 100 gal.)	
Car weight - empty	25 200 kg (55 600 lb.)	
Car weight - full	119 300 kg (263 000 lb.)	
Tank		
Material	Aluminum Alloy	
Thickness	14.3 mm (9/16 in.)	
Inside diameter	2.40 m (94-1/2 in.)	
Test pressure	690 kPa (100 psi)	
Burst pressure	3450 kPa (500 psi)	
Typical Dimensions		
Coupled length	13.6 m (44 ft. 7-1/4 in.)	
Length over strikers	12.8 m (41 ft. 11-3/4 in.)	
Length of truck centres	9.46 m (31 ft. 1/4 in.)	
Height to top of grating	3.48 m (11 ft. 5-13/16 in.)	
Overall height	4.26 m (13 ft. 11-13/16 in.)	
Overall width (over grabs)	3.21 m (10 ft. 6-1/2 in.)	
Coupler height over rail	0.88 m (2 ft. 10-1/2 in.)	
Length of grating	2.44 m (8 ft. 1/8 in.)	
Width of grating	1.83 m (6 ft.)	
Loading/Unloading Fixtures		
Unloading connection	51 mm (2 in.)	
Fill hole	203 mm (8 in.)	
Air connection	25 mm (1 in.)	
Bottom outlet		prohibited, CTC approval
Bottom washout	152-203 mm (6-8 in.)	required for bottom unloading
Safety Devices		
Safety vent		required, may be equipped with frangible disc with 3 mm (1/8 in.) vent hole
Insulation		Optional
Dome		None

TABLE 4 DRUMS

Type of Drum	Designation	Description	Figure No. (if any)
Steel (lined for sodium hypochlorite service)	1A1	Nonremovable head, reusable	2
	1A1A	1A1 with reinforced chime	2
	1A1B	1A1 with welded closure flange	2
	1A1C	1A1 with lead coating	2
	1A1D	1A1 with coating (other than lead)	2
	1A3	Nonremovable head, single use only	2
Plastic	1H1	Nonremovable head. Maximum capacity 250 L (55 gal.). Maximum net mass 400 kg (882 lb.)	
Steel Drums with inner plastic receptacles	6HA1	Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity 225 L (49 gal.)	

FIGURE 2

SODIUM HYPOCHLORITE **TYPICAL DRUM CONTAINER**

Typical steel drum (LINED FOR SODIUM HYPOCHLORITE)

MIN. 2.4mm
LEAD COATING FOR
IAIC DESIGNATION

CONTENTS LABEL

BODY AND HEADS
CONSTRUCTED OF
ROLLED STEEL

MAX. CAPACITY
250 L

MAX. NET MASS
400 kg

85 cm

53 cm
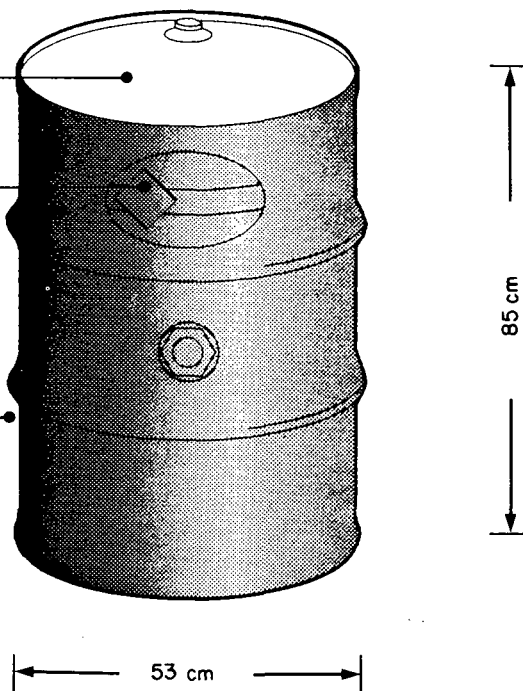
Glass carboys, boxed or in expanded polyethylene containers, are also used to transport sodium hypochlorite (TDGC 1980). Polyethylene containers are widely used for smaller quantities. Commercial swimming pool grades (12-15 percent) are often sold in 3.8 and 7.6 L (0.8 and 1.5 gal.) bottles, 23-57 L (5-12.5 gal.) carboys and 205 L (45 gal.) drums. All of these containers are constructed solely of polyethylene (Kirk-Othmer 1978).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (PC 1982):

- The storage tank must be checked to make sure that it will hold the contents of the car.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution placards displayed.
- A safe operating platform must be provided at the unloading point.

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

- Connect the 51 mm (2 in.) unloading line to the discharge outlet and connect the 25 mm (1 in.) air line. Air pressure must be reduced to 207 kPa (30 psi) for unloading. A safety relief valve must be installed in the air line to release at 242 kPa (35 psi).
- After opening the air supply valve, the unloading connection valve can then be opened to unload the car.
- Once the car is empty, the air supply valve must be closed and the vent valve in the air line opened to allow the line pressure to equalize to atmospheric pressure.
- Reverse the above procedure to close up the car.

4.2.2 Off-loading Equipment and Procedures for Tank Motor Vehicles. The unloading of sodium hypochlorite tank trailers is similar to that of railway tank cars described above.

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

Schedule 40 seamless ASTM A106 carbon steel pipes and welding fittings lined with glass, rubber or polyvinylidene chloride (Saran) are recommended for sodium

hypochlorite service (DCRG 1978). Flanged joints should be used and these should be welded, because threaded pipe fittings tend to leak. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipeline should be tested with air at pressures from 345 to 518 kPa (50-75 psi) and all leaks carefully stopped. The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on these tank cars; however, process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended (PC 1982). Outdoor lines must be self-draining.

Stainless steel pipe and swivel joints may be used for flexible sections. Either the ball bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance. Flexible hose constructed of fluorine rubber (Viton) may be used at normal temperatures and low concentrations (GF).

For valving, quick acting ball or plug valves in "20" alloy will serve adequately (JSSV 1979). Viton may be used as a gasket material (GF). A single-suction centrifugal pump with "20" alloy shaft and impeller and a cast stainless steel casing is recommended for pumping. Stainless steel storage tanks or rubber-lined carbon steel tanks are commonly used. Fibre-reinforced plastic or PVC-lined steel may be used as well (SH 1977).

4.3 Compatibility with Materials of Construction

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

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 5   COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical Conc.	Temp. (°C)	Material of Construction Recommended	Conditional	Not Recommended
1. Pipes and Fittings	>15%	23	PE (DPPED 1967)		ABS (DPPED 1967)

TABLE 5   COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (cont'd)	5, 15%	52	PVDC (DCRG 1978)		
		60	PVC I PVC II (DPPED 1967)		
	5%	79	PP (DCRG 1978)		
		93	Chlorinated Polyether (DCRG 1978)		
		135	PVDF (DCRG 1978)		
	15%	79	Chlorinated Polyether PP (DCRG 1978)		
		135	PVDF (DCRG 1978)		
	Conc.	To operating limit of material	PVC I PE (MWPP 1978) Kynar (Kirk-Othmer 1978)		ABS (MWPP 1978)
2. Valves	5% and over solution	>50	Alloy "20" SS 316 (subject to pitting around stem) (JSSV 1979)		
			Teflon-lined ball valves, Kynar-lined diaphragm valves (Kirk-Othmer 1978)		
3. Pumps	5%, 10%	49	GRP with FPM "O" Ring		
			High Silicon Cast Iron (HIS 1969)		

TABLE 5   COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
4. Storage	>15%	>50	CS glass-lined CS PVC-lined CS rubber-lined (SH 1977)		CS Copper (SH 1977)
5. Others	5%	20	SS 316 (ASS)	SS 302 SS 304 (ASS)	SS 410 SS 430 (ASS)
	Diluted (Aqueous)	20	uPVC IIR EPDM FPM CSM (GF)	PE PP (GF)	POM NR NBR CR (GF)
	Conc.	23	PP (TPS 1978)		
		49		PP (TPS 1978)	
		60	PVC (TPS 1978)		
		66			PP (TPS 1978)
		85	CPVC (TPS 1978) Si SBR (GPP)		
	10%	24 to 100	Glass (CDS 1967)		
	Conc.	24 to 100	Glass (CDS 1967)		
	10%	24	Concrete (CDS 1967)		Wood (CDS 1967)
	Conc.	24	Concrete (CDS 1967)		

TABLE 6   MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Cast Iron, High Silicon
	Chlorinated Polyether

TABLE 6   MATERIALS OF CONSTRUCTION (Cont'd)

Abbreviation	Material of Construction
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene) Rubber
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
GRP	Glass Reinforced Vinyl Ester
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (Followed by grade, if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride (Saran)
PVDF	Polyvinylidene Fluoride
Si	Silicon
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
SS (Followed by grade)	Stainless Steel
	"20" Alloy (Durimet 20, Carpenter 20)
uPVC	Unplasticized Polyvinyl Chloride
	Wood (Fir)

5 CONTAMINANT TRANSPORT

5.1 General Summary

Sodium hypochlorite is normally produced and marketed as an aqueous solution of 5 to 15 percent. Sodium hypochlorite solutions are slightly denser than water at 20°C. When spilled in water, they will mix rapidly. When spilled on soil, the liquid will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may be an environmental concern.

Because sodium hypochlorite solutions are essentially nonvolatile, dispersion in air is not a problem. Chlorine produced as a result of reaction or heat can be a problem but is difficult to predict.

The following factors are considered for the movement of a sodium hypochlorite spill in water and soil:

```
                          ┌─ Leak from ──────────────── ┌─ Rate of discharge
                          │   tank                       │
                          │                              └─ Percent remaining
                          │
Contaminant ─────────────┤── Water ──────────────────────── Diffusion and downstream
Transport                 │                                  concentration
                          │
                          └─ Soil ───────────────────────── Depth and time
                                                             of penetration
```
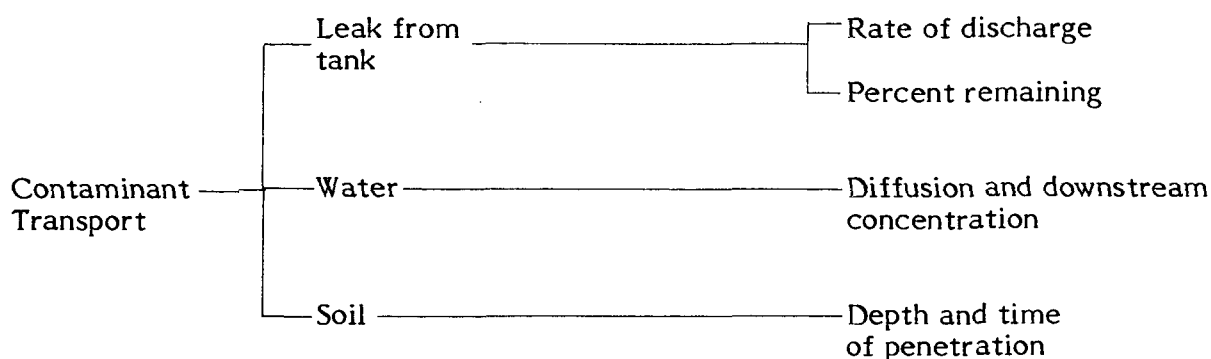
It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction.
Sodium hypochlorite solutions are commonly transported in tank trucks and less commonly in railway tank cars as nonpressurized liquids. While the capacities of the tanks vary widely, one tank size, with a capacity of about 80 000 L, has

been chosen for development of the leak nomograms. This size has been chosen throughout the EnviroTIPS series to allow for comparisons.

If a tank car loaded with sodium hypochlorite solution is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the relatively low volatility of sodium hypochlorite solutions and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.
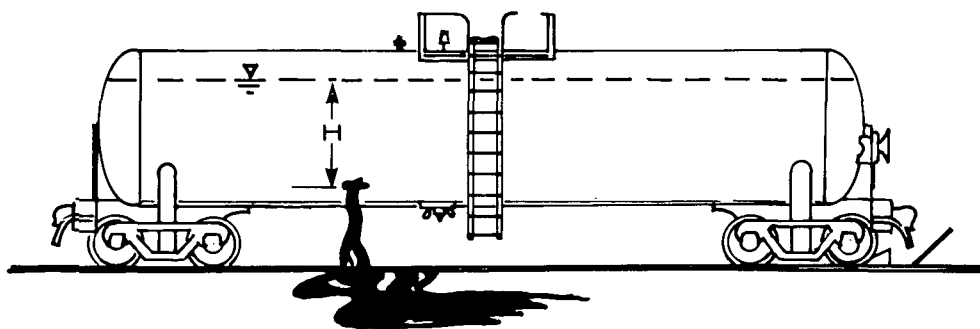
FIGURE 3   TANK CAR WITH PUNCTURE HOLE IN BOTTOM

The rate of outflow (q) from a vent hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). It is a function of the hole size (A) and shape, the height of the liquid above the puncture (H), and a coefficient of discharge (Cd).

As the gravitational force predominates over viscous and other forces for a wide range of fluid conditions, the rate of discharge is relatively independent of fluid temperature and viscosity (Rouse 1961). Consequently, it is reasonable to assume a constant discharge coefficient for sodium hypochlorite for a wide range of temperature and viscosity. For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

5.2.2   Nomograms.

5.2.2.1   Figure 4:   Percent remaining versus time. Figure 4 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

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

5.2.2.2 Figure 5: Discharge rate versus time. Figure 5 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car (2.75 m ϕ x 13.4 m long) filled with sodium hypochlorite has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution of Problem A

• Use Figure 4
• With t = 10 min and d = 150 mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

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

Solution to Problem B

• Use Figure 5
• With t = 10 min and d = 150 mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

Because sodium hydrochlorite solutions are nonvolatile in foreseeable spill circumstances, there is no significant potential for dispersion in the air.

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, sodium hypochlorite solutions will mix rapidly. Mixing allows the spill to be diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In

FIGURE 4

SODIUM HYPOCHLORITE

**PERCENT REMAINING
VS TIME**

Equivalent Diameter of Puncture

50 mm
100mm
150 mm
200 mm
250 mm
300 mm
350 mm
400 mm
450 mm
500 mm

Percent Remaining %

Time from Puncture (min)
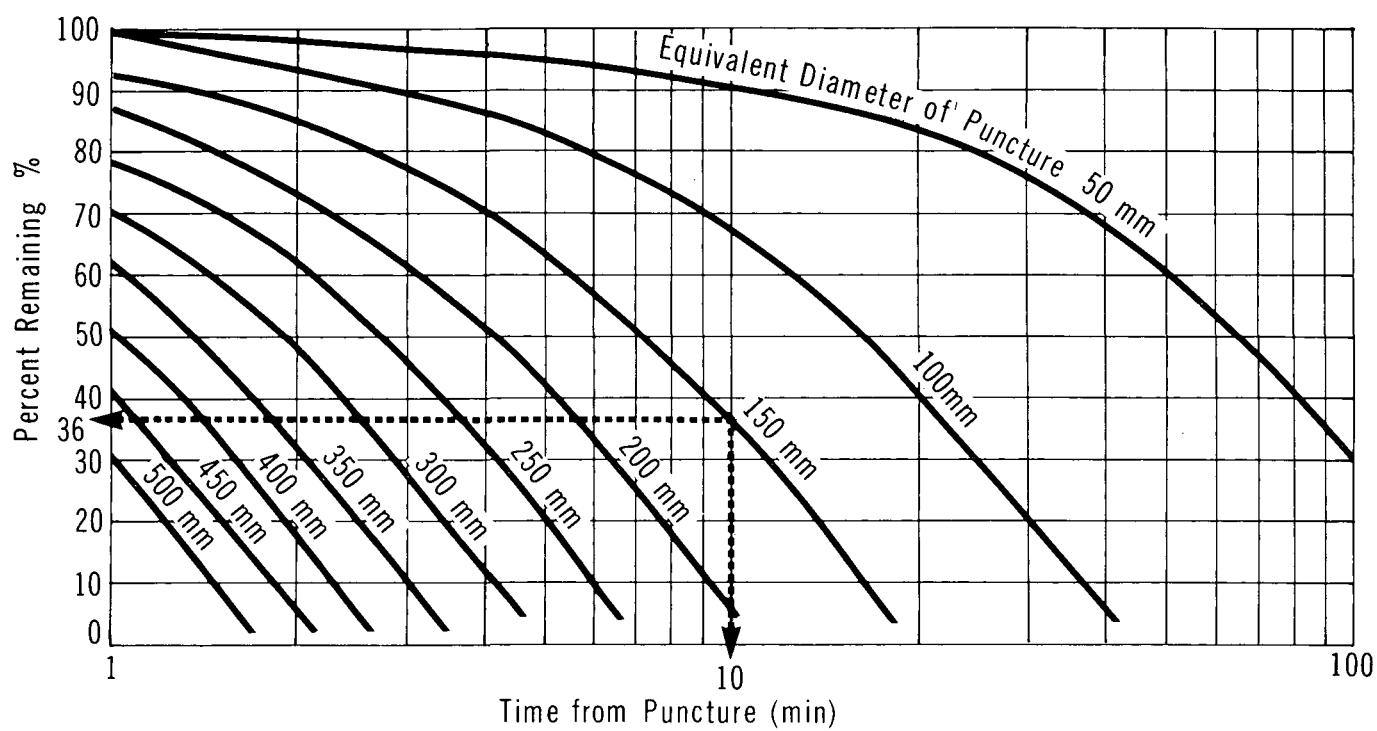
FIGURE 5

SODIUM HYPOCHLORITE

**DISCHARGE RATE
VS TIME**

Equivalent Diameter of Puncture

500 mm
450 mm
400 mm
350 mm
300 mm
250 mm
200 mm
150 mm
100 mm
50 mm

Discharge (L/s)

Time from Puncture (min)
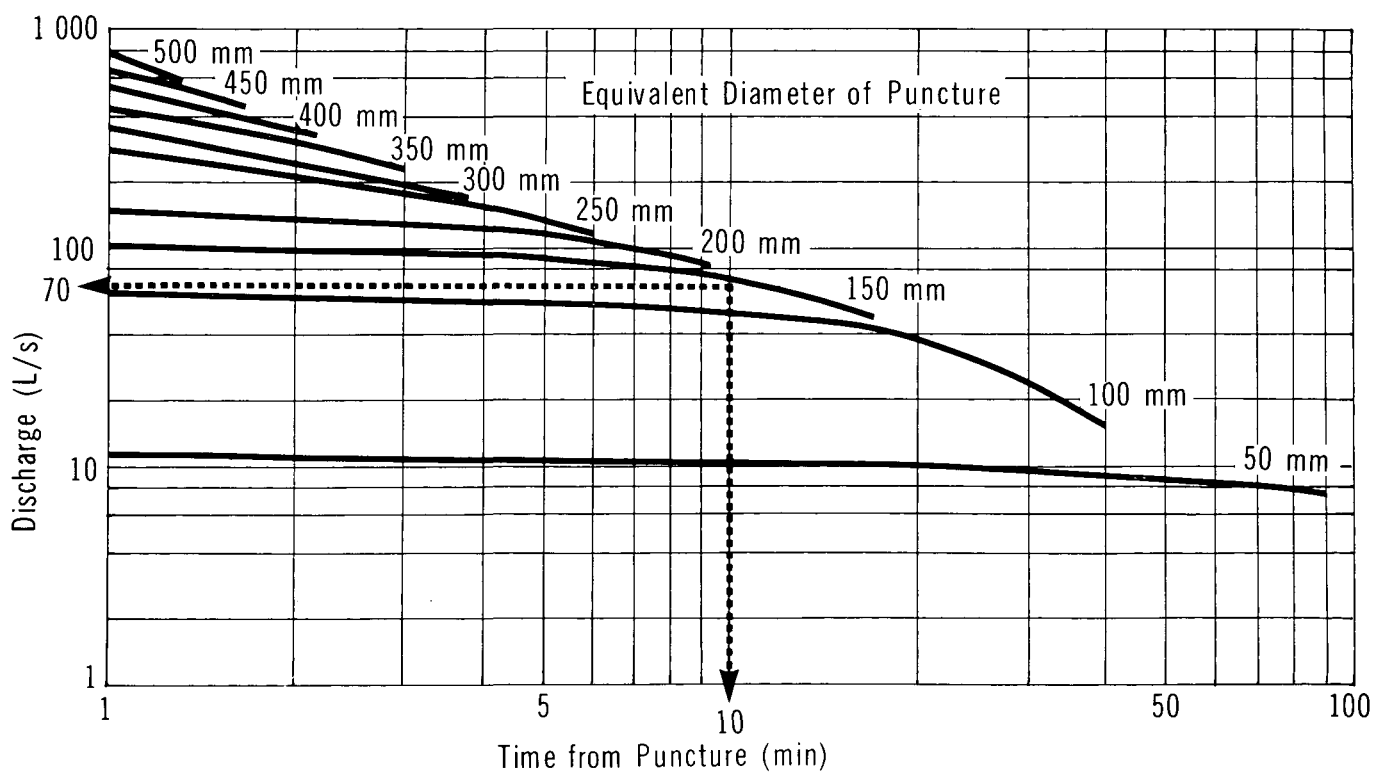
rivers, the principal mixing agent is stream turbulence while in calm water mixing takes place by molecular diffusion.

To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The 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).

<u>Non-tidal Rivers</u>

Figure 7:	time versus distance for a range of average stream velocities
Figure 8:	hydraulic radius versus channel width for a range of stream depths
Figure 9:	diffusion coefficient versus hydraulic radius for a range of average stream velocities
Figure 10:	alpha* versus diffusion coefficient for various time intervals
Figure 11:	alpha versus delta* for a range of spill sizes
Figure 12:	maximum concentration versus delta for a range of river cross-sectional areas

<u>Lakes or Still Water Bodies</u>

Figure 13:	volume versus radius for the hazard zone for a range of lake depths
Figure 14:	average concentration versus volume for the hazard zone for a range of spill sizes

The flowchart in Figure 6 outlines the steps required to estimate the downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 7 through 14) are described in the following subsections.

---

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

SODIUM HYPOCHLORITE

**FLOW CHART TO DETERMINE POLLUTANT
CONCENTRATION IN NON-TIDAL RIVERS**

```
            ┌─────────┐
            │  SPILL  │
            └─────────┘
```

| DEFINE PARAMETERS |
| STREAM WIDTH (W) |
| STREAM DEPTH (d) |
| AVERAGE VELOCITY (U) |
| SPILL MASS |
| DOWNSTREAM DISTANCE (X) |

Step 1: Observed or Estimated

W = _____ m

d = _____ m

U = _____ m/s

MASS = _____ tonnes

X = _____ m

CALCULATE TIME (t) TO
REACH POINT OF INTEREST

Step 2: Use Figure 7

t = _____ minutes

CALCULATE HYDRAULIC
RADIUS (r) OF CHANNEL

Step 3: Use Figure 8

r = _____ m

CALCULATE LONGITUDINAL
DIFFUSION COEFFICIENT (E)

Step 4: Use Figure 9

E = _____ m²/s

CALCULATE ALPHA (α)
AT TIME (t)

Step 5: Use Figure 10

α = _____

CALCULATE DELTA (Δ)
FOR SPILL MASS

Step 6: Use Figure 11

Δ = _____

COMPUTE A = W × d

Step 7: Compute stream cross-sectional
Area (A)
A = W × d _____ m²

CALCULATE MAXIMUM CONCENTRATION (C)

FOR STREAM CROSS-SECTIONAL AREA (A)

Step 8: Use Figure 12

C = _____ ppm

5.4.2.1 Nomograms for non-tidal rivers.

Figure 7: Time versus distance. Figure 7 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be readily obtained from Figure 7.

Figure 8: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 8 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 9: Diffusion coefficient versus hydraulic radius. Figure 9 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 8 and the average stream velocity (U).

Figure 10: Alpha versus diffusion coefficient. Figure 10 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 11: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated for Figure 11 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 12: Maximum concentration versus delta. Figure 12 represents the final step of 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 12 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water. Since sodium hypochlorite solutions are not much denser than water, the effect here is presumed to be slight.

5.4.2.2 Nomograms for lakes or still water bodies.

Figure 13: 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

SODIUM HYPOCHLORITE

TIME vs DISTANCE

Distance, X (m)

FIGURE 8
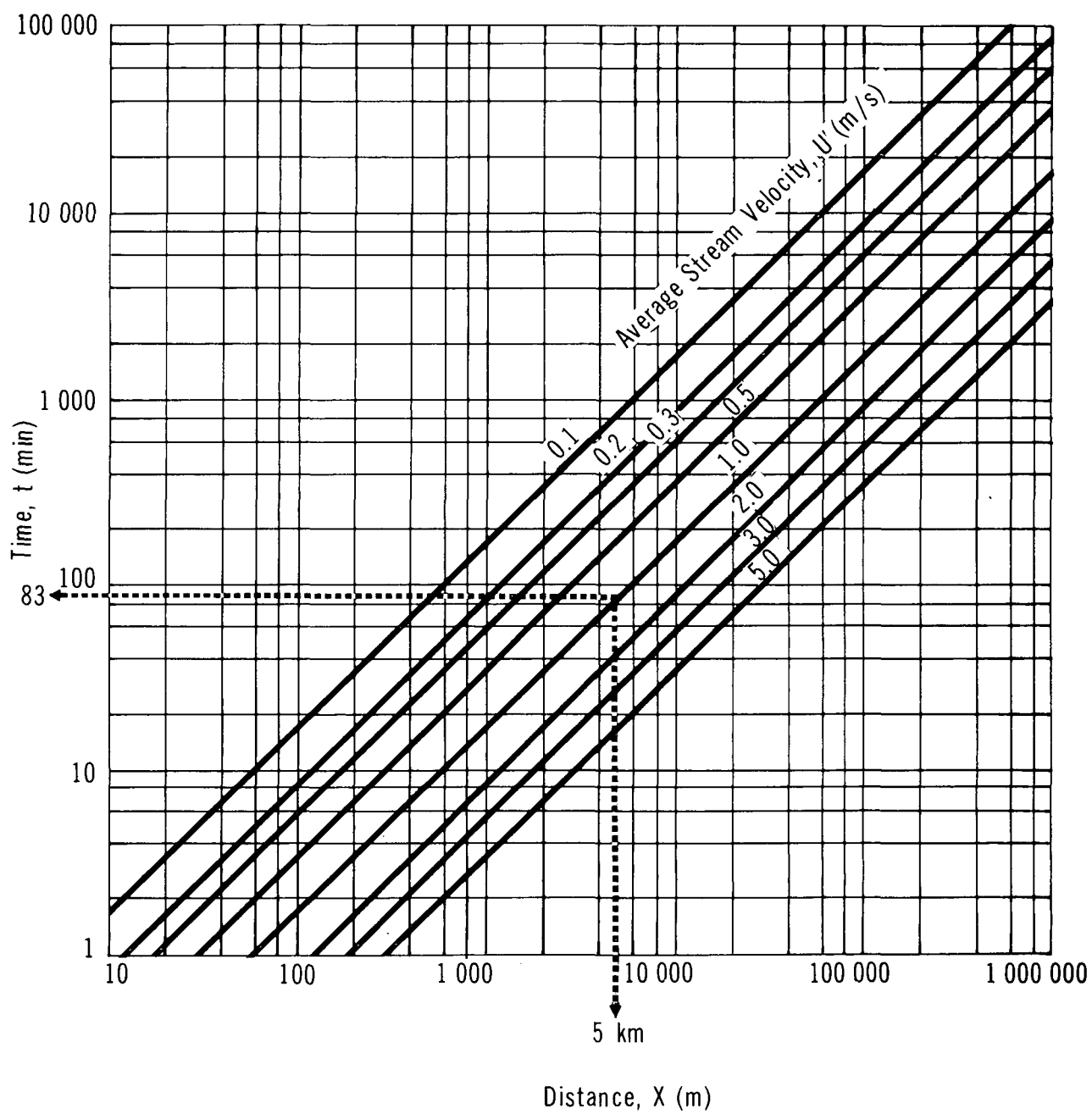
SODIUM HYPOCHLORITE

**HYDRAULIC RADIUS VS
CHANNEL WIDTH**

FIGURE 9
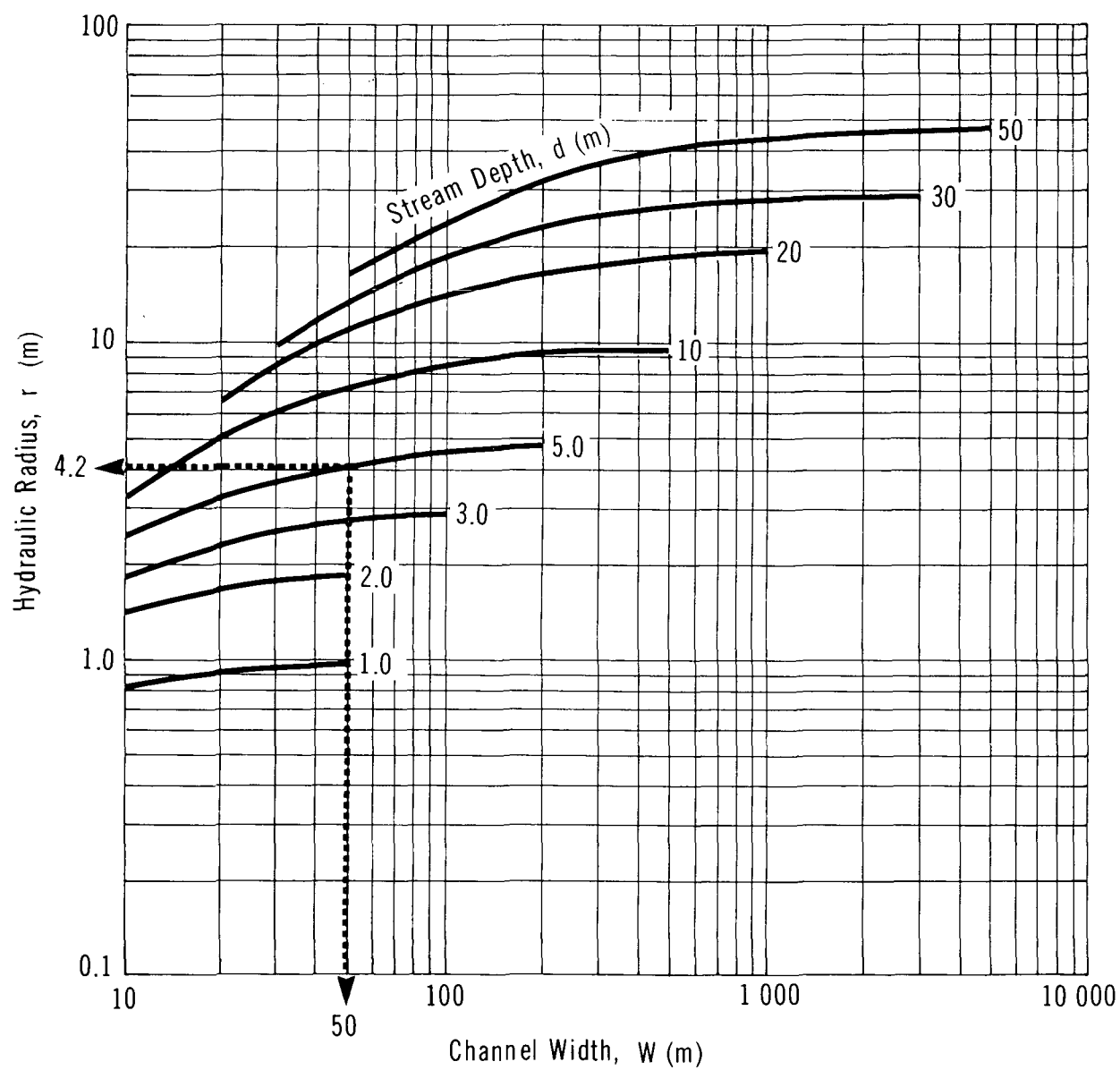
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Diffusion Coefficient, E (m²/s) vs Hydraulic Radius, r (m), with curves for Average Stream Velocity, U (m/s): 5.0, 3.0, 2.0, 1.0, 0.5, 0.3, 0.2, 0.1, 0.05, 0.03, 0.02, 0.01
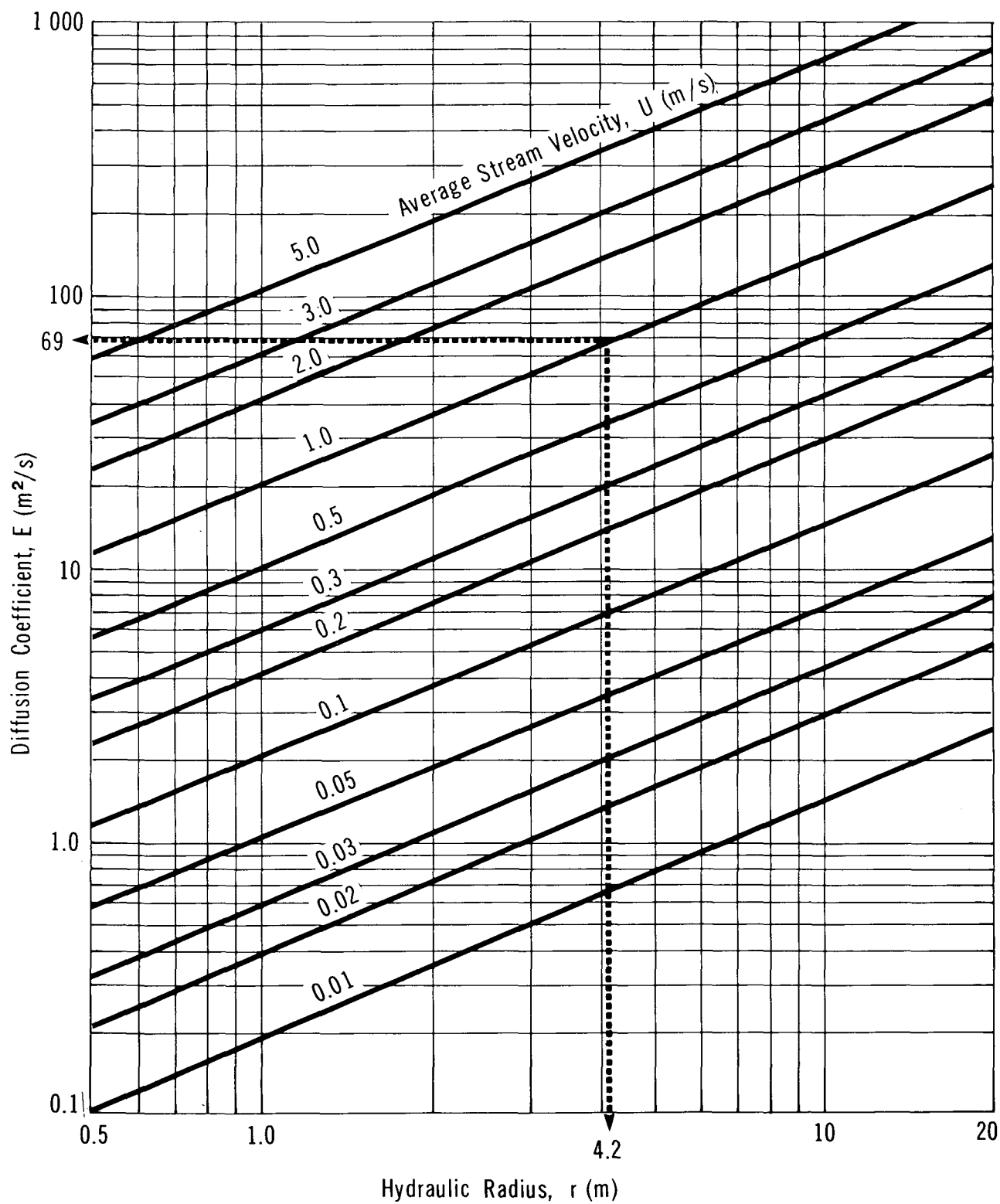
SODIUM HYPOCHLORITE

ALPHA vs DIFFUSION COEFFICIENT

Diffusion Coefficient, E (m²/s)
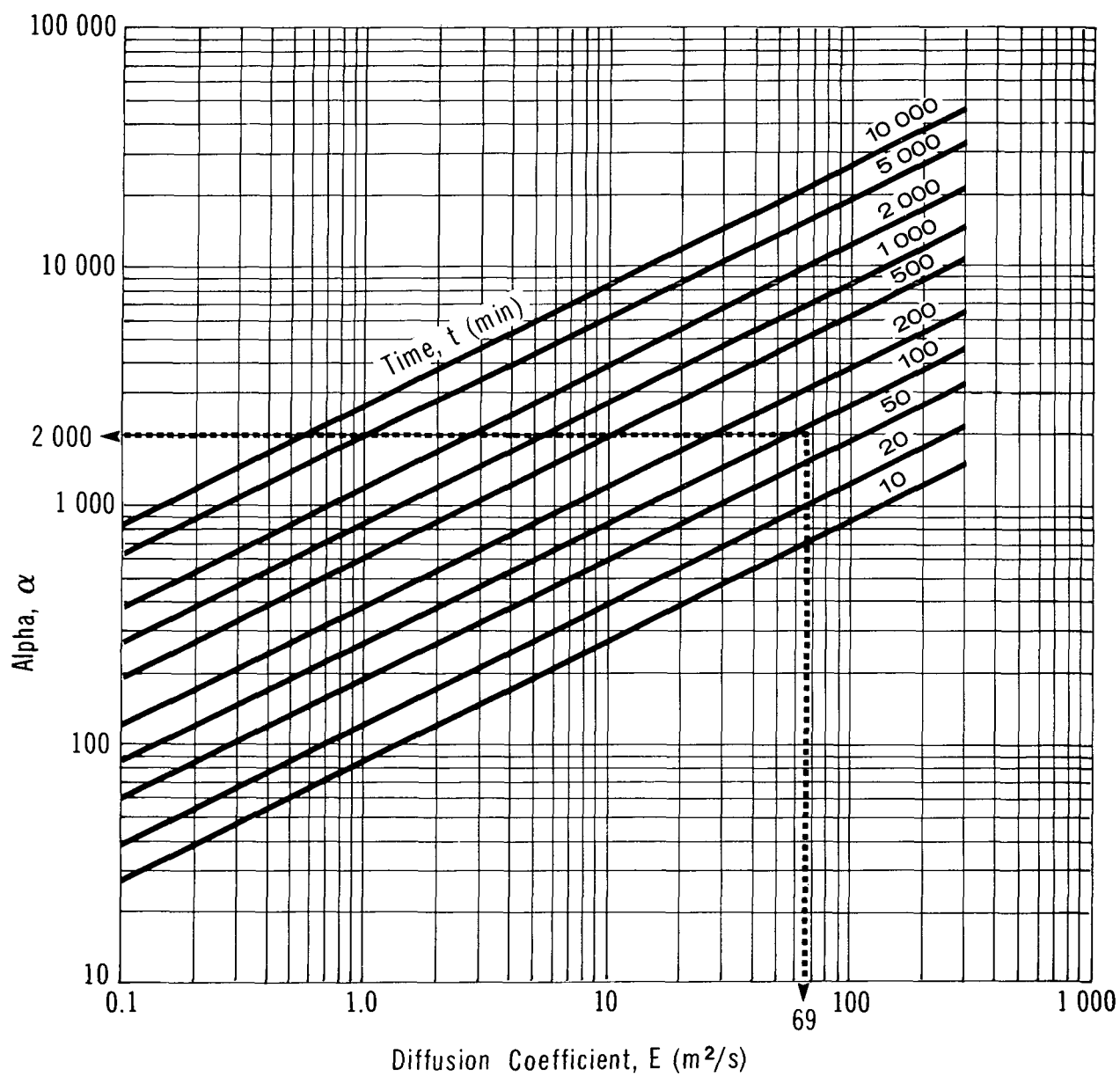
SODIUM HYPOCHLORITE

ALPHA vs DELTA
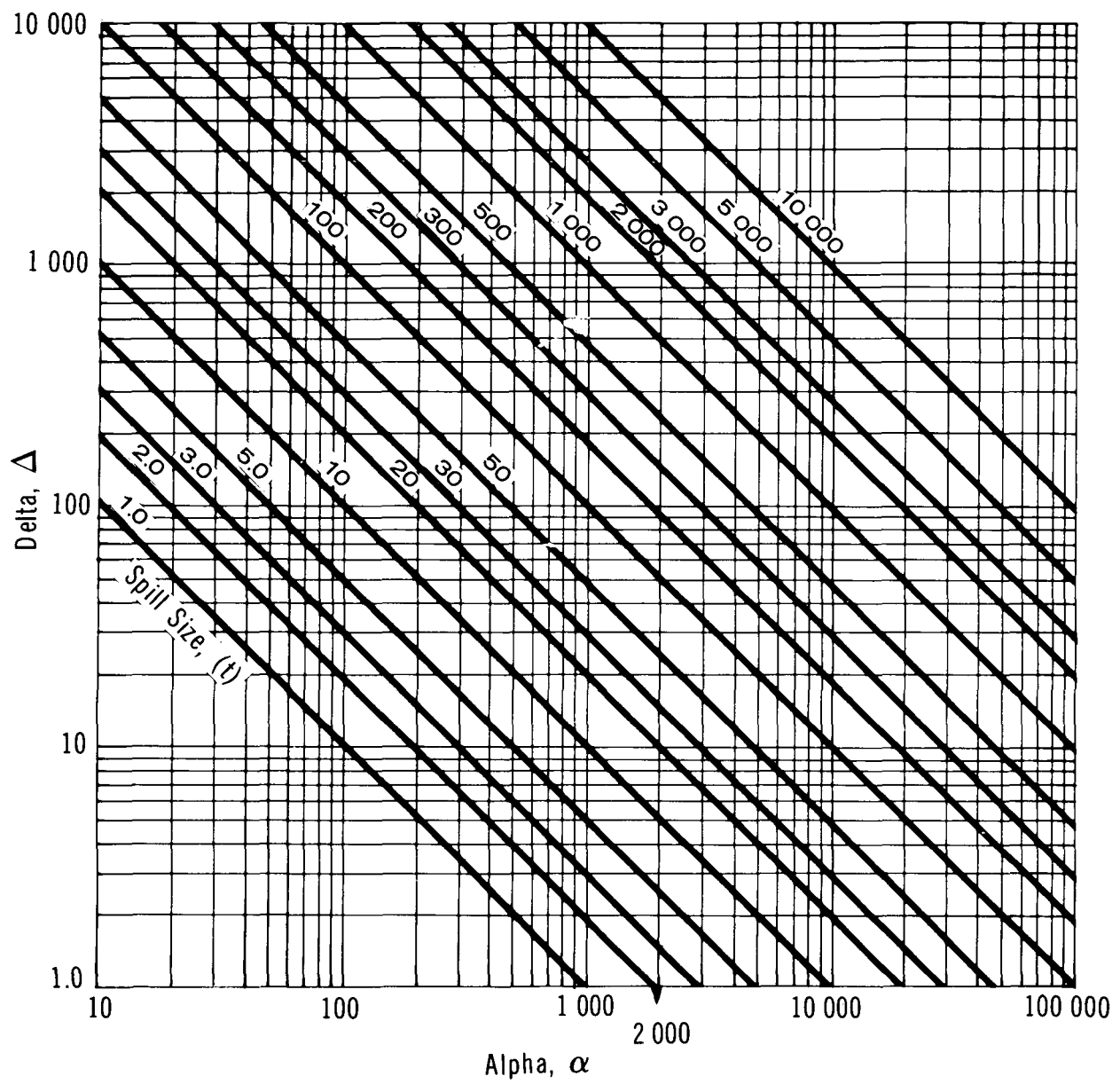
SODIUM HYPOCHLORITE

MAXIMUM CONCENTRATION vs DELTA
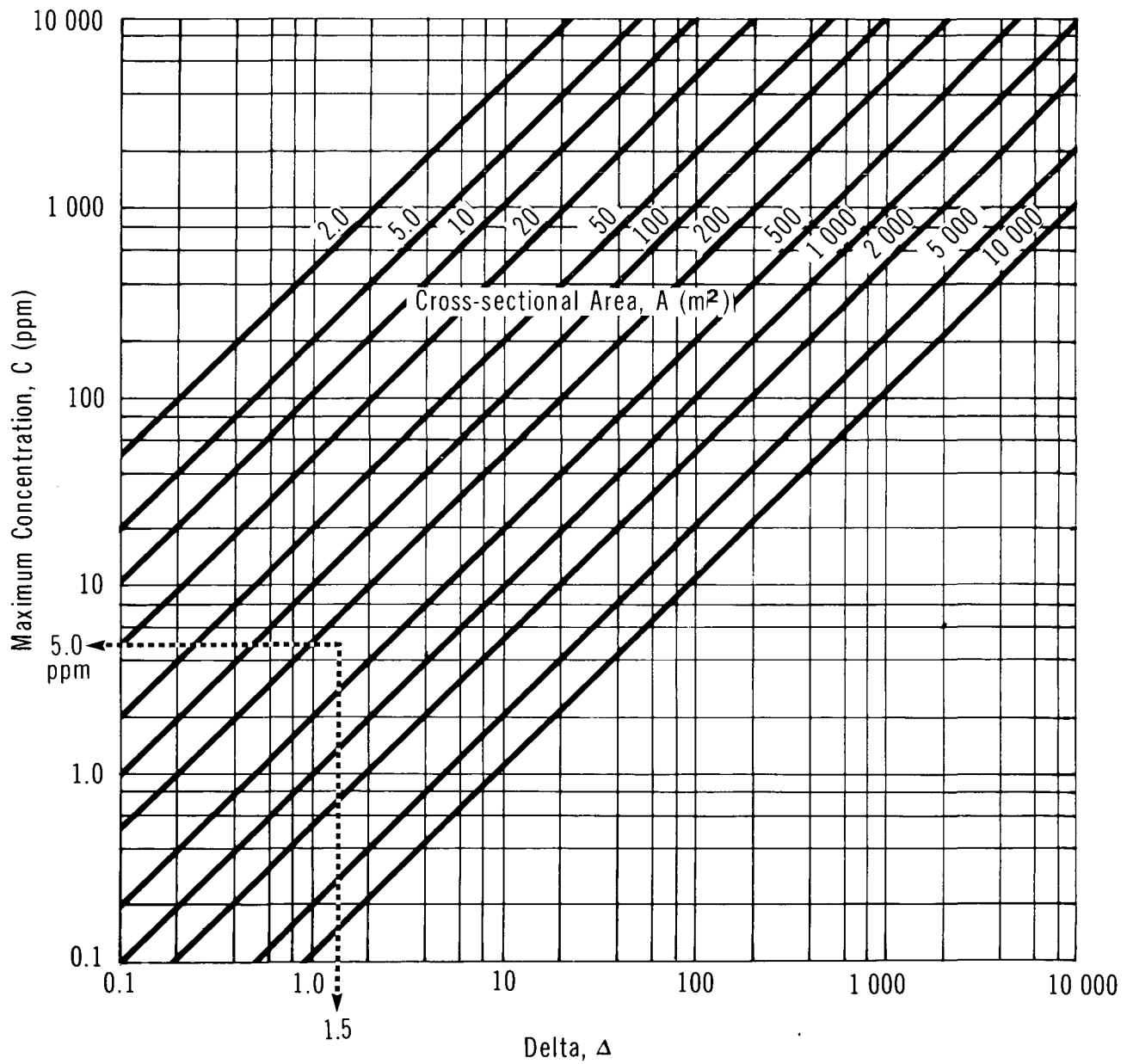
SODIUM HYPOCHLORITE

VOLUME vs RADIUS
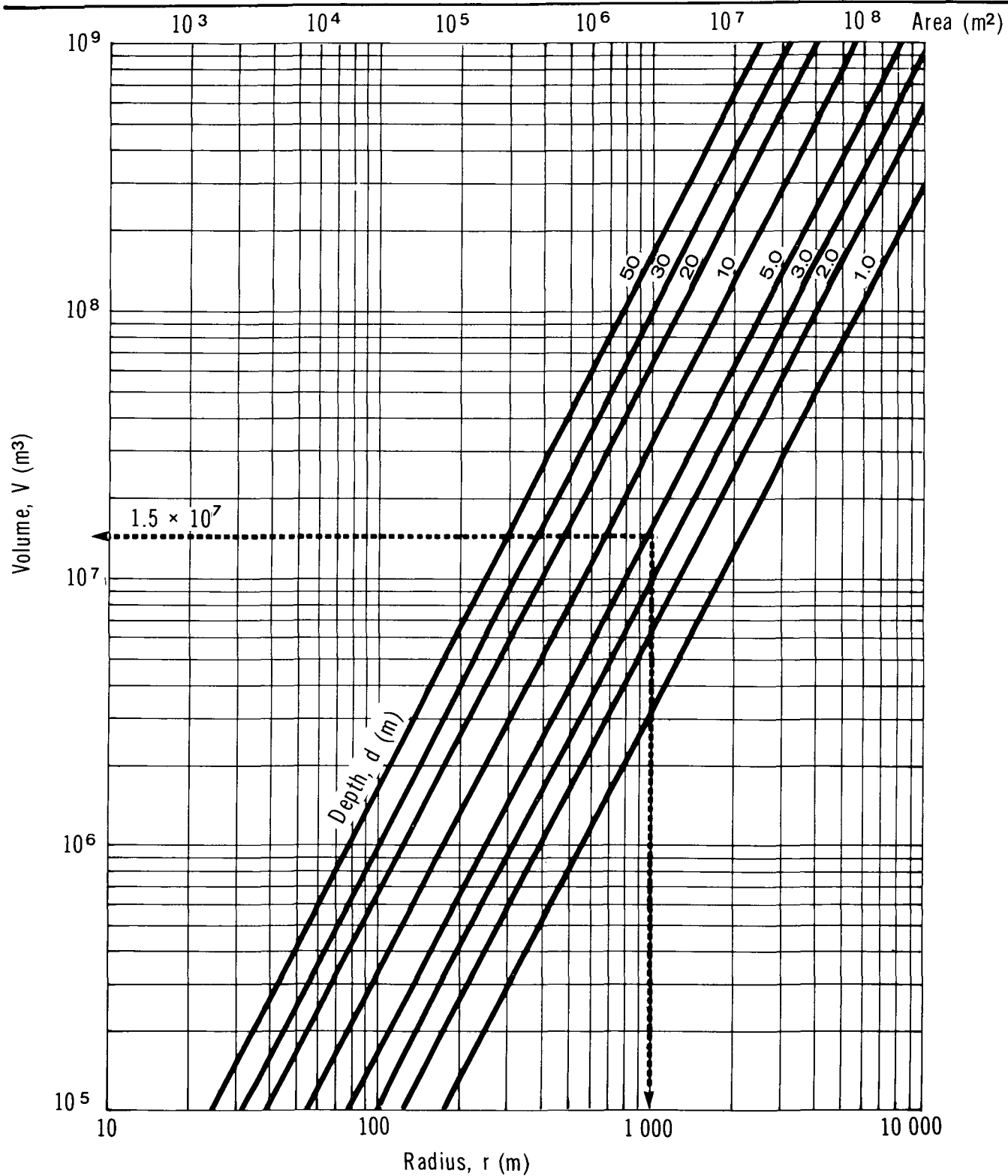
the cylinder can be obtained from Figure 13. The radius (r) represents the distance from the spill to the point of interest.

Figure 14: 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 14 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3   Sample Calculations.

5.4.3.1   Pollutant concentration in non-tidal rivers.
A 20 tonne spill of 15 percent sodium hypochlorite solution has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1:   Define parameters
- W = 50 m
- d = 5 m
- U = 1 m/s
- spill mass = 20 tonnes of 15 percent sodium hypochlorite solution, equivalent to 3 tonnes of sodium hypochlorite

Step 2:   Calculate the time to reach the point of interest
- Use Figure 7
- With X = 5000 m and U = 1 m/s, t = 83 min

Step 3:   Calculate the hydraulic radius (r)
- Use Figure 8
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4:   Calculate the longitudinal diffusion coefficient (E)
- Use Figure 9
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5:   Calculate alpha (α)
- Use Figure 10
- With E = 69 m^2/s and t = 83 min, α = 2000

FIGURE 14

SODIUM HYPOCHLORITE

AVERAGE CONCENTRATION vs VOLUME
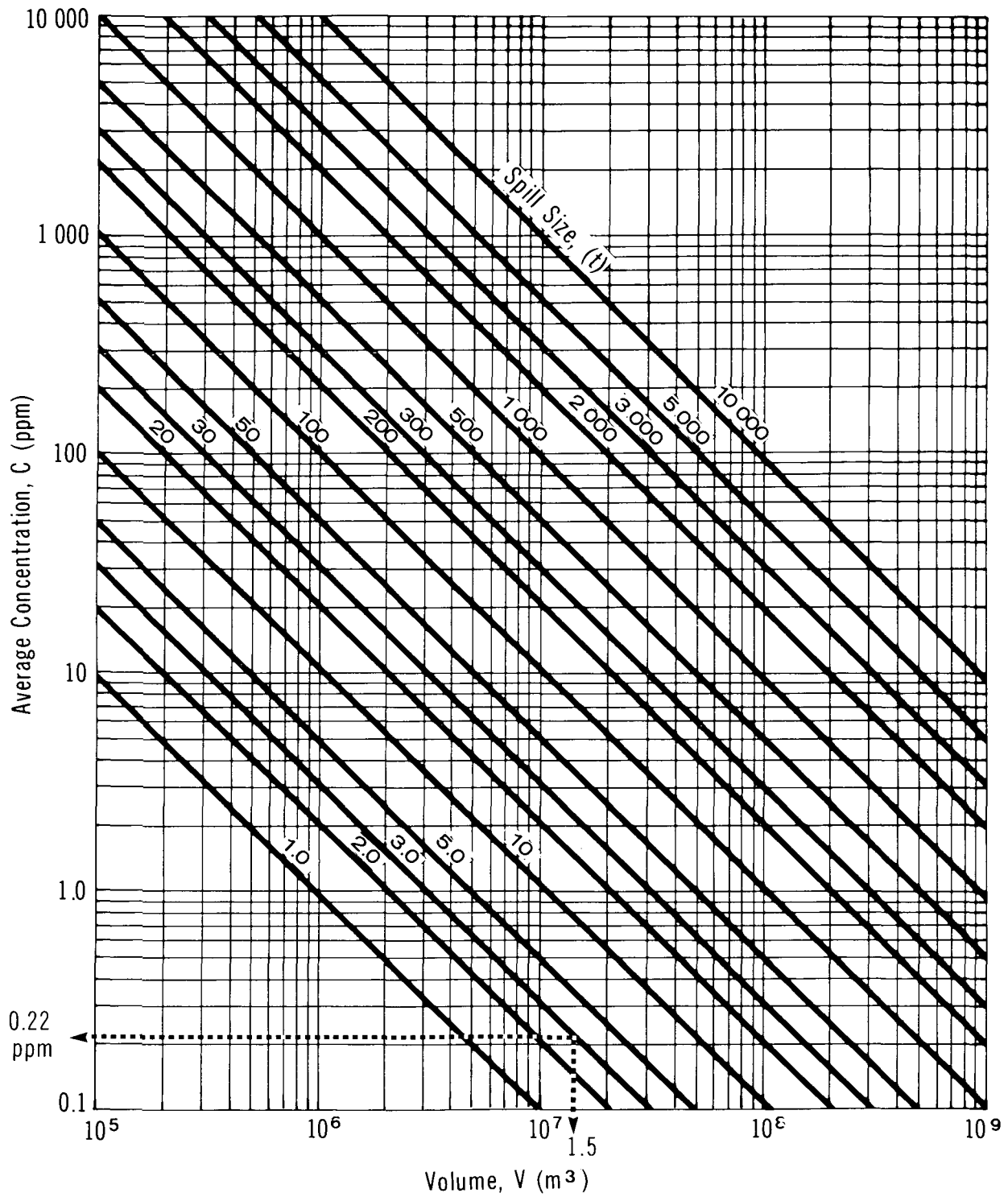
Step 6:   Calculate delta (Δ)
- Use Figure 11
- With alpha (α) = 2000 and spill mass = 3 tonnes, delta (Δ) = 1.5

Step 7:   Compute the stream cross-sectional area (A)
- A = W x d = 50 x 5 = 250 m^2

Step 8:   Calculate the maximum concentration (C) at the point of interest
- Use Figure 12
- With Δ = 1.5 and A = 250 m^2, C = 5 ppm

5.4.3.2   Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of 15 percent sodium hypochlorite has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1:   Define parameters
- d = 5 m
- r = 1000 m
- spill mass = 3 tonnes (equivalent weight of sodium hypochlorite)

Step 2:   Determine the volume of water available for dilution
- Use Figure 13
- With r = 1000 m, d = 5 m, the volume is approximately 1.5 x 10^7 m^3

Step 3:   Determine the average concentration
- Use Figure 14
- With V = 1.5 x 10^7 m^3 and spill mass = 3 tonnes, the average concentration is 0.22 ppm

5.5   Subsurface Behaviour: Penetration into Soil

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

When spilled onto soil, some of the chemical may be lost to decomposition; the balance will infiltrate the soil. Since sodium hypochlorite solutions are miscible with water, the presence of water in the soil or falling as precipitation at the time of the spill will influence the rate of chemical movement in the soil. Dilution through mixture with water will decrease the viscosity more than the mass density. This will have the net effect of increasing the penetration velocity to become similar to that of water. If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off into adjacent areas.

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

Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with diffusion and dispersion serving to reduce the acid concentration somewhat. This is shown schematically in Figure 15.

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

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

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

where: k = intrinsic permeability of the soil (m^2)

ρ = mass density of the fluid (kg/m^3)

μ = absolute viscosity of the fluid (Pa·s)

g = acceleration due to gravity = 9.81 m/s^2

The fluids are sodium hypochlorite in various concentrations, and water. Because of a lack of data on the viscosity of sodium hypochlorite solutions, only calculations for water are presented. These are applicable to dilute solutions of sodium hypochlorite.

SODIUM HYPOCHLORITE   **SCHEMATIC SOIL TRANSPORT**

Spill-Zone

Water Table

Contaminant Plume

Direction of Flow →
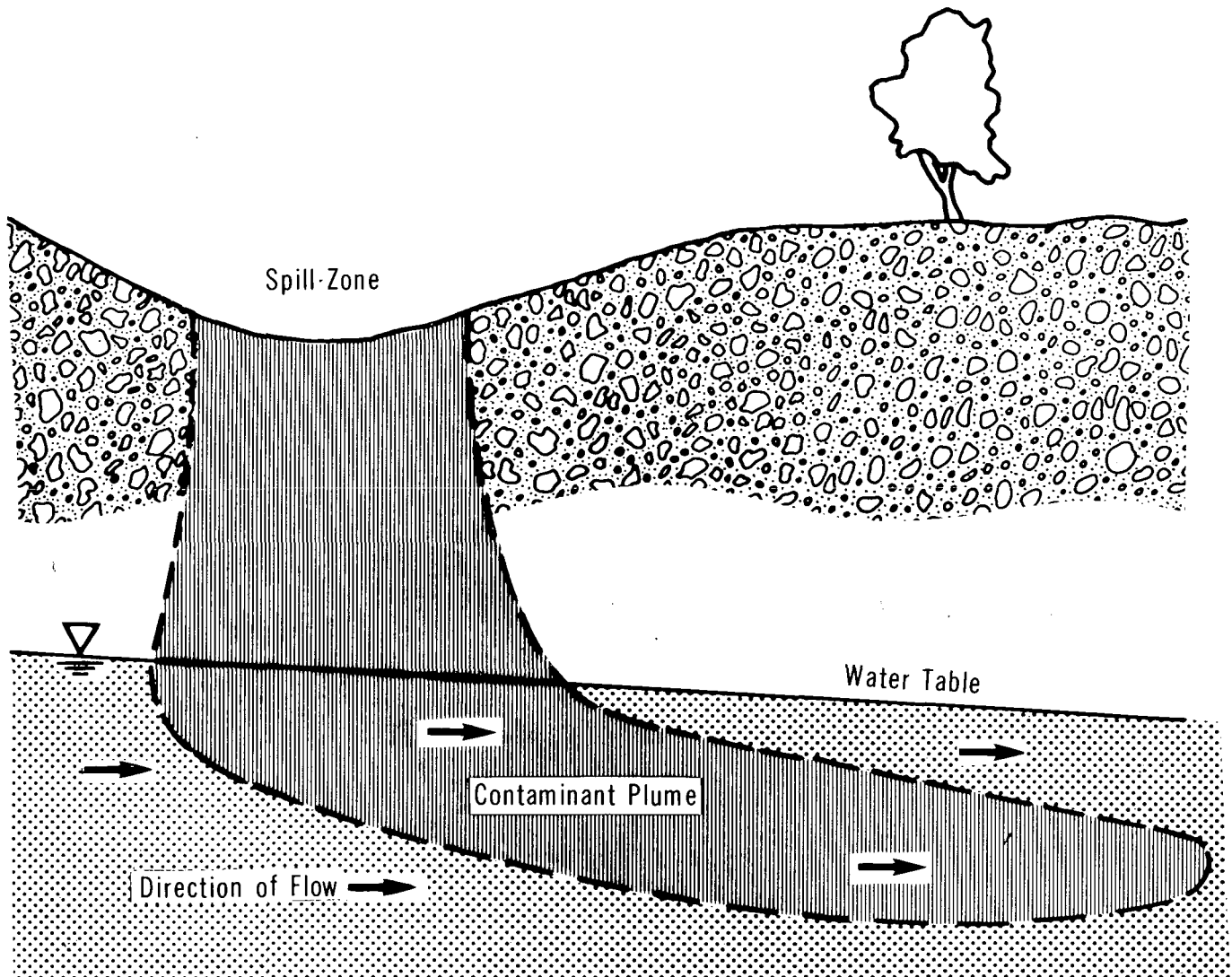
Soil: Coarse Sand
- Porosity (n) = 0.35
- Intrinsic Permeability (k) = 10^{-9} m^2
- Field Capacity (θ_{fc}) = 0.075

Property	Water	
	4°C	20°C
Mass density (ρ), kg/m^3	1000	998
Absolute viscosity (μ), Pa·s	1.57×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(0.63 \times 10^7)k$	$(0.98 \times 10^7)k$

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

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

5.5.5   Penetration Nomograms. Nomograms for the penetration of sodium hypochlorite solutions into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p. A flowchart for the use of the nomograms is presented in Figure 16. The nomograms are presented as Figures 17, 18 and 19.

5.5.6   Sample Calculation. A 20 tonne spill of dilute sodium hypochlorite solution has occurred on silty sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 8 days after the spill.

FLOWCHART FOR NOMOGRAM USE

Spill

↓

Identify concentration

Step 1

| Estimate time (t_p) elapsed since spill | Define soil type
• coarse sand
• silty sand
• clay till | Estimate soil and liquid temperature |

Step 2

Calculate area of spill (A)

Step 3

Obtain penetration depth (B) in time (t_p) from Figure 17–19

PENETRATION IN COARSE SAND

Time of Penetration, t_p (min)

Depth of Penetration, B (metres)

Diluted, 4°C

Diluted, 20°C

FIGURE 18
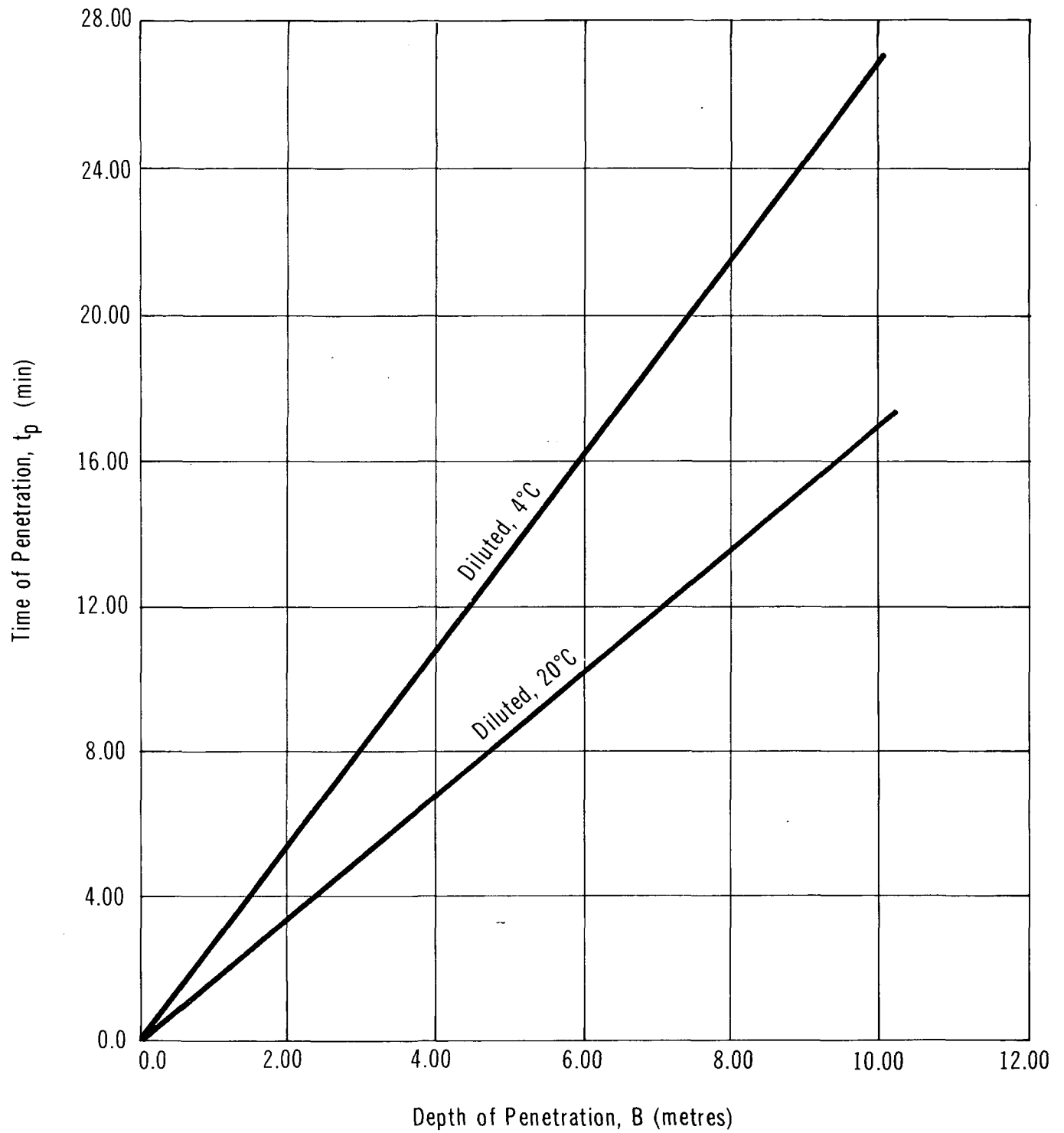
SODIUM HYPOCHLORITE

PENETRATION IN SILTY SAND

Depth of Penetration, B (metres)

PENETRATION IN CLAY TILL
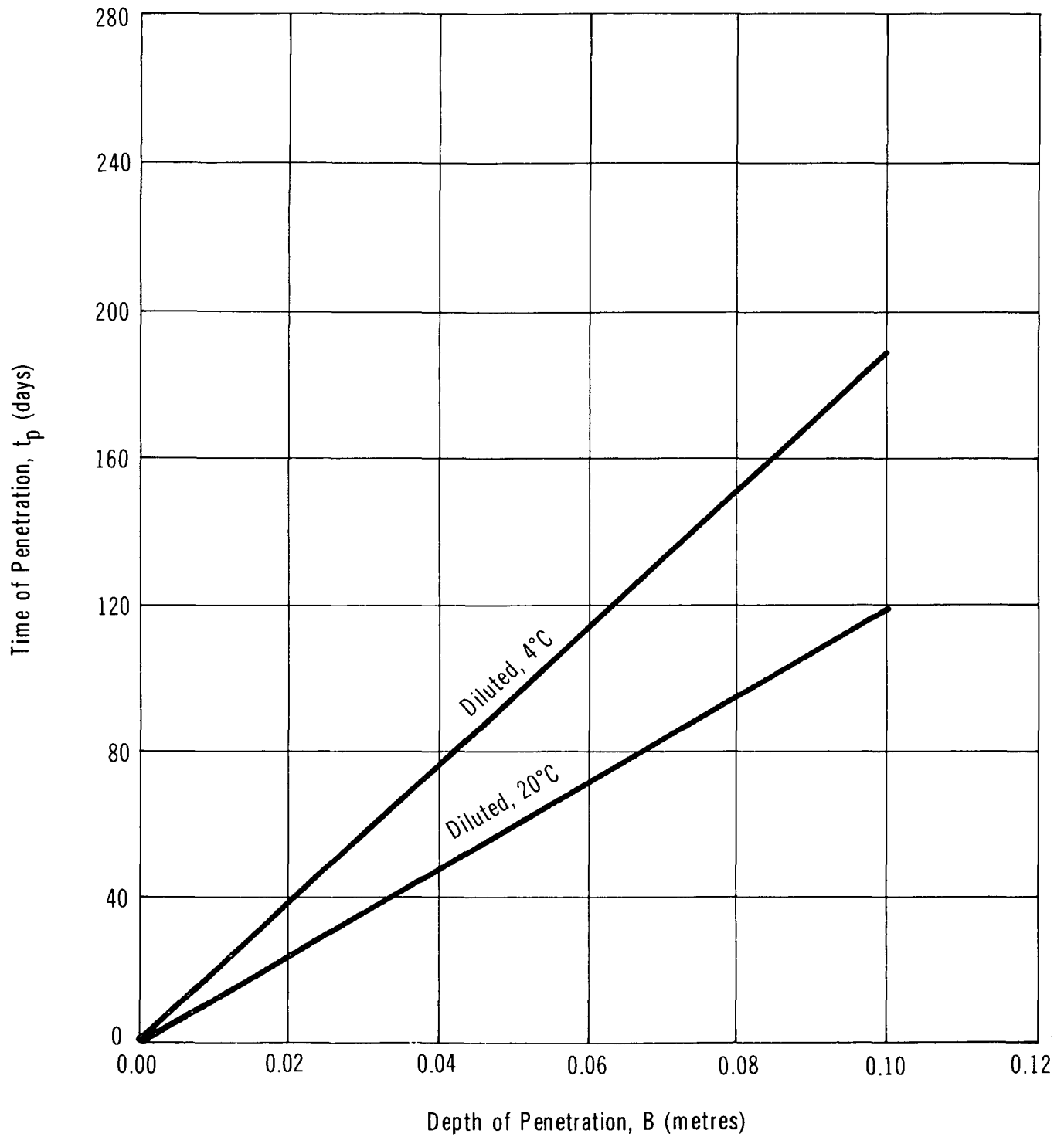
<u>Solution</u>

Step 1:   Define parameters

    •   Mass spilled = 20 000 kg (20 tonnes)

    • $T = 20°C$

    • $r = 8.6$ m

    •   Soil = silty sand

    •   Groundwater table depth (d) = 13 m

    •   Time since spill (t_p) = 8 d

Step 2:   Calculate the area of spill

    • $A = \pi r^2 = 232$ m^2

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

    •   For silty sand, $B = 6.8$ m at $t_p = 8$ d

    •   Groundwater table has not been reached in this time

6   ENVIRONMENTAL DATA

6.1   Suggested or Regulated Limits

6.1.1   Water. Sodium hypochlorite concentration in drinking water is not regulated; however, the chlorine objectives apply. Ontario has stated a chlorine objective as 2 µg/L (Water Management Goals 1978).

In the United States, the Environmental Protection Agency has suggested an average of 3 µg/L as a maximum for protection of freshwater aquatic life, with peaks up to 50 µg/L once a day (WQC 1972). Several states have guidelines, with 2-5 µg/L being the range for aquatic life protection, 2-10 µg/L for ambient waters and 2-5 µg/L for water supply (API 1980).

6.1.2   Air. Not specifically applicable; however, hypochlorites may release chlorine, which is regulated at 300 µg/m^3 in Ontario (Ontario E.P. Act 1971).

6.2   Aquatic Toxicity

6.2.1   U.S. Toxicity Rating. The toxicity rating for chlorine is applicable here; for chlorine, the TL_m96 assigned is less than 1 ppm (RTECS 1979).

6.2.2   Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Kill Data					
0.5 (calcium hypochlorite)	tns	Trout	killed	-	WQC 1963
Fish Toxicity Tests					
5.9 to 8.0	96	Fathead minnow	LC_{50}	static, pH 7.2-7.9 HD 40-48, 22°C	JWPCF 1982

Microorganisms

Hypochlorites are commonly used as bactericides; algae are affected at levels of 2 ppm (EPA 440/9-75-009). A safety limit of 0.1 mg/L has been determined in one study; 0.02 mg/L residual chlorine was found to inhibit phytoplankton growth by 50 percent (Magazzu 1976).

Conc. (mg/L)	Time (hours)	Species	Result	Reference
Invertebrates				
52	96	Grass shrimp	LC_{50}	OHM-TADS 1981

6.3 Effect Studies

If sodium hypochlorite is considered as a chlorine source, toxicities cited range as low as 0.03 ppm chlorine in water. Bactericidal action will interfere with biological patterns in receiving waters (EPA 440/9-75-009).

6.4 Degradation

Sodium hypochlorite is an oxidizing agent and does not have a B.O.D. or C.O.D. potential. It will gradually change into salt and oxygen or, more probably, be consumed by contact with soil or waterborne organic matter in a few days. It may interfere with sewage treatment organisms in much the same way as chlorine (OHM-TADS 1981).

6.5 Long-term Fate and Effects

Sodium hypochlorite is not persistent in the environment and has no potential for bioaccumulation or food chain contamination (OHM-TADS 1981).

7   HUMAN HEALTH

Very little toxicity information is available for sodium hypochlorite. No standards for exposure to the substance and no reviews of toxicity were encountered in the literature. The majority of data concern toxic effects due to household exposures and ingestion of sodium hypochlorite. No data concerning teratogenic or carcinogenic effects of exposure to the compound were encountered, although there was one report of a completed mutagenicity test. The compound is not listed in EPA TSCA Inventory. The toxicological data summarized here have been extracted from reliable standard reference sources.

It should be noted that chlorine is released by sodium hypochlorite solutions. This process is increased with increasing temperature or with reaction with acids. The inhalation toxicity briefly referred to in this section is that of chlorine; sodium hypochlorite does not exist outside of aqueous solutions of low percentage. It should also be noted that most sodium hypochlorite solutions contain small amounts of sodium hydroxide, which would affect its ingestion toxicity.

7.1   Recommended Exposure Limits

No exposure standards for sodium hypochlorite were found in the literature.

7.2   Irritation Data

7.2.1   Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Skin contact may cause vesicular eruptions and eczematoid dermatitis	TDB (on-line) 1981
Unspecified	Skin irritation with blistering and eczema	ITII 1981

7.2.2   Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Liquid can be irritating to the eyes if contact is maintained	CHRIS 1978
SPECIES: Rabbit		
1 drop (15 percent solution at pH 11.2)	Caused immediate severe pain, hemorrhages from the conjunctiva and nose; rapid onset of ground glass appearance of corneal epithelium, followed by moderate bluish edema of the cornea; chemosis; neovascularization of the conjunctiva; scarring of the nictitating membrane	TDB (on-line) 1981
Unspecified (5 percent solution at pH 11.1 to 11.6)	Caused immediate pain, but if washed off with water within 30 seconds, left only slight transient corneal epithelial haze and conjunctival edema, with return to normal within a day or less	TDB (on-line) 1981

7.3   Threshold Perception Properties

7.3.1   Odour.

Odour characteristics: Chlorine-like (TDB (on-line) 1981).

7.3.2   Taste. No data.

7.4   Toxicity Studies

7.4.1   Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
Unspecified	Corrosive and irritating via inhalation	TDB (on-line) 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
Unspecified	Aspiration pneumonitis occurs in 8.1 percent of ingestions. Hematemesis is common with large ingestion	TDB (on-line) 1981
Unspecified	This compound interacts with the acid milieu of the stomach, producing hypochlorous acid which has irritant properties to the mucous membranes and skin	Doull 1980
Unspecified	Ingestion of a lethal intoxication dose had a corrosive effect and methemoglobinemia was present	TDB (on-line) 1981
SPECIES: Dog		
Unspecified	Undiluted liquid bleach (Chlorox) instilled into upper esophagus of dogs produced no permanent esophageal lesions unless lower end of esophagus was occluded, in which case half the animals died from esophageal perforation, mediastinitis and pleurisy	TDB (on-line) 1981
SPECIES: Rabbit		
Unspecified	Undiluted liquid bleach (Chlorox) instilled into upper esophagus produced no permanent esophageal lesions	TDB (on-line) 1981

7.4.3 Mutagenicity, Teratogenicity and Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Hamster		
500 mg/L (27 h)	Cytogenic analysis, using hamster lung cells. No interpretation provided	RTECS 1979

7.5   Symptoms of Exposure

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

7.5.1   Inhalation.

1.   Irritation of nose and throat (ITII 1981).
2.   Cough (ITII 1981).
3.   Corrosive to tissue (TDB (on-line) 1981).
4.   Pneumonitis.
5.   Pulmonary edema (ITII 1981).
6.   Shock.

7.5.2   Ingestion.

1.   Pain and inflammation of the mouth, pharynx, esophagus and stomach.
2.   Blistering in the throat (ITII 1981).
3.   Vomiting.
4.   Mediastinitis or peritonitis (TDB (on-line) 1981).
5.   Erosion of mucous membranes (TDB (on-line) 1981).
6.   Edema of pharynx, glottis and larynx with stridor and obstruction (TDB (on-line) 1981).
7.   Perforation of esophagus or stomach (ITII 1981).
8.   Hemorrhage.
9.   Circulatory collapse.
10. Cyanosis (TDB (on-line) 1981).
11. Delirium.
12. Coma.

7.5.3   Skin Contact.

1.   Irritation.
2.   Blistering.
3.   Eczema.
4.   Vesicular eruptions (TDB (on-line) 1981).

7.5.4   Eye Contact.

1.   Irritation.

7.6   Human Toxicity to Decay or Combustion Products

Sodium hypochlorite solutions release chlorine when heated above 35°C (TDB (on-line) 1981).

7.6.1   Chlorine. Chlorine is a greenish-yellow, noncombustible gas at atmospheric pressure; it has a suffocating odour detectable at a threshold of 3.5 ppm by volume. Concentrations around 5 ppm cause respiratory complaints, inflammation of the mucous membranes of the nose, and increased susceptibility to tuberculosis in workers chronically exposed. Acute exposures to higher concentrations can cause eye and nose irritation and pulmonary edema. The TLV® is 1 ppm and the STEL is 3 ppm (TLV 1983).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Sodium Hypochlorite 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		•		•									Decomposes, releases chlorine upon heating	Bretherick 1979
SPECIFIC CHEMICALS														
Ammonium Acetate			•										Within a few seconds	NFPA 1978
Ammonium Carbonate			•										Within a few seconds	NFPA 1978
Ammonium Nitrate			•										Within a few seconds	NFPA 1978
Ammonium Oxalate			•										Within a few seconds	NFPA 1978
Ammonium Phosphate			•										Within a few seconds	NFPA 1978
Aziridine	•												Explosive N-chloro compound is formed	Bretherick 1979
Methanol	•													Bretherick 1979
Phenylacetonitrile	•												Probable formation of nitrogen trichloride	Bretherick 1979

8.1 Compatibility of Sodium Hypochlorite 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
Urea			•										Formation of nitrogen tri-chloride	NFPA 1978
CHEMICAL GROUPS														
Acids						•	•						Releases chlorine	Gokhale 1978
Alkali and Alkaline Earth Metals	•		•										Hydrogen gas can be formed	EPA 600/2-80-076
Amines			•										N-mono or di-chloroamines are formed	Bretherick 1979
Catalytic Metals			•			•							Decomposes, releasing oxygen with finely divided or soluble metal salts (e.g., Co, Ni)	Gokhale 1978
Epoxides	•		•											EPA 600/2-80-076
Esters	•												Hydrolysis occurs	EPA 600/2-80-076
Explosives	•		•											EPA 600/2-80-076

8.1 Compatibility of Sodium Hypochlorite 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
Halogenated Organics	•		•										Flammable olefins or acetylenes may be formed	EPA 600/2-80-076
Isocyanates	•			•	•									EPA 600/2-80-076
Ketones	•													EPA 600/2-80-076
Metal Powders, Vapours and Sponges	•	•	•										Hydrogen gas can be formed	EPA 600/2-80-076
Nitro Compounds		•											Dry salts are explosive	EPA 600/2-80-076
Organophosphates	•	•											Explosive re-arrangement from thiono to thiolo form may occur from hydrolysis	EPA 600/2-80-076
Polymerizable Compounds	•													EPA 600/2-80-076
Toxic Metals										•				EPA 600/2-80-076

9   COUNTERMEASURES

9.1   Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, discrepancies between different sources of information may occur. It is recognized that counter-measures 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. Sodium hypochlorite is a nonflammable material. It reacts with acids, releasing chlorine gas (Olin MSDS 1980).

9.1.2   Fire Extinguishing Agents. Sodium hypochlorite is not combustible. Fire fighting agents can be chosen on the basis of other materials present.

9.1.3   Evacuation. Evacuate all people to a distance of at least 60 m upwind and 300 m downwind of the spill (OHMS-TADS 1981).

9.1.4   Spill Actions, Cleanup and Treatment.

9.1.4.1   General. Stop or reduce discharge of material if this can be done without risk (Olin MSDS 1980). Avoid skin contact and inhalation of chlorine.

9.1.4.2   Spills on land. Contain if possible. Remove as much material as possible with pumps or vacuum equipment; absorb residual material on sand or other noncombustible absorbent material and shovel into containers for disposal (ERG 1980).

9.1.4.3   Spills in water. For treatment of contaminated water, gravity separation of solids followed by reduction with a bisulphite salt (solution should be acidified with sulphuric acid to pH of 2.0 or 3.0) and neutralization with soda ash (pH of 10.0) is recommended. The sodium will precipitate out as sodium sulphate. Prior to discharge, the effluent is neutralized with hydrochloric acid to pH 7.0 (EPA 600/2-77-227).

A number of process treatments have been used to convert sodium hypochlorite to less harmful products (Gokhale 1978). Catalysts, such as cobalt in the form of dilute cobalt salt solutions (best at pH 11-18, 38-42°C), reduce the sodium hypochlorite as follows:

$$NaOCl \xrightarrow{\text{catalyst}} NaCl + 1/2\ O_2$$
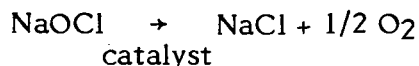
A nickel-ion catalyst will function if higher amounts of NaOH are present. A sulphite treatment such as:

$$NaOCl + Na_2SO_3 \rightarrow Na_2SO_4 + NaCl$$
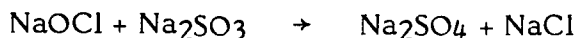
has also been used to reduce sodium hypochlorite.

9.1.5   Disposal. Waste sodium hypochlorite solutions must never be discharged into sewers or surface waters. Following treatment, either at the spill site or at a waste management facility, the resultant sludge may be disposed of to a secure landfill.

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

If the spilled material is known to be sodium hypochlorite:

- Safety goggles, impervious clothing and NIOSH/MSHA-approved self-contained breathing apparatus should be worn (OHM-TADS 1981; Olin MSDS 1980).
- Rubber or neoprene is recommended for gloves and boots (Olin MSDS 1980).
- Eye wash stations and safety showers should be readily available in areas of use and in spill situations (Olin MSDS 1980).

9.1.7   Storage Precautions. Do not store near organic materials. Solutions of sodium hypochlorite are corrosive to metals and tissue (OHM-TADS 1981).

10   PREVIOUS SPILL EXPERIENCE

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

11   ANALYTICAL METHODS

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

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

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

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

11.1   Quantitative Methods for the Detection of Sodium Hypochlorite in Air

Sodium hypochlorite is not a stable solid and thus will not exist in air. Chlorine, however, is released by the solutions, especially when heated. Methods for measuring chlorine appear in the chlorine EnviroTIPS manual.

11.2   Quantitative Methods for the Detection of Sodium Hypochlorite in Water

11.2.1   Iodometric Method (AWWA 1965). Concentrations of 0.04 mg/L free chlorine to saturation can be determined. A representative sample volume of 1 L is collected for readings of 1 mg/L or less, 500 mL for readings between 1 and 10 mg/L, and proportionally less for higher predicted readings.

Place 5 mL of acetic acid or sufficient to reduce sample solution to pH 3 or 4. Add 1 g potassium iodide and mix. Add 0.025 N or 0.01 N thiosulphate solution (prepared from $Na_2S_2O_3 \cdot 5H_2O$) until the yellow colour of the liberated iodine is almost discharged (solution almost clear). Add 1 mL starch solution (5 g starch into 1 L boiling water, let settle, use only clear portion) and titrate with the thiosulphate solution until the blue colour just disappears.

The free chlorine is calculated from the following:

$$mg/L \ Cl = \frac{(A \pm B) \times N \times 35\ 450}{\text{sample volume (in mL)}}$$

where   A   =   mL titrant for sample

            B   =   mL titrant for blank

            N   =   normality of thiosulphate solution used

11.2.2 Flame Photometry (ASTM 1979). Concentrations greater than 1 mg/L (ppm) of sodium hypochlorite as sodium may be determined by flame photometry. A minimum of 2 L of representative sample is collected in an appropriate container. A suitable volume of sample is atomized into the flame of a suitable flame photometer and the emission intensity determined at 589 nm. The sample concentration is determined using a calibration curve. The sample value should be corrected to eliminate other sources of sodium (e.g., NaCl, NaOH) in the sample solution.

11.3 Qualitative Method for the Detection of Sodium Hypochlorite in Water

Sodium hypochlorite as sodium in water may be determined by a flame test. The sample is collected as in Section 11.2.2. A clean platinum wire is dipped into a portion of sample and placed in the hottest part of a bunsen burner flame. A bright yellow, intense flame indicates sodium (Welcher 1955).

11.4 Quantitative Method for the Detection of Sodium Hypochlorite in Soil

11.4.1 Flame Photometry (Hesse 1972). A variable range of concentrations of sodium hypochlorite as sodium in soil may be determined depending on the aliquot of extract atomized into a suitable flame photometer. A 2 mm, 5 g soil sample, accurately weighed, is placed in a 50 mL narrow neck centrifuge tube. A 30 mL volume of 0.5 M magnesium acetate solution is added, and the tube is stoppered and centrifuged for 5 minutes at 400 rev/s. The supernatant is decanted into a 100 mL volumetric flask. The extraction is repeated twice more and the extracts combined in the volumetric flask. The combined extracts are diluted to volume with 0.5 M magnesium acetate. A suitable aliquot of sample is atomized into the flame of a suitable flame photometer and the emission intensity determined at 589 nm. The sample concentration is determined using a calibration curve. A blank sample of uncontaminated soil should also be run to determine the background concentration in the area; this value should be subtracted from any true sample reading.

11.5   Qualitative Method for the Detection of Sodium Hypochlorite in Soil

Sodium hypochlorite as sodium in soil may be determined by a flame test. The sample is collected and extracted as in Section 11.2.2. A clean platinum wire is dipped into a portion of sample and placed in the hottest part of a bunsen burner flame. A bright yellow, intense flame indicates sodium (Welcher 1955).

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EnviroTIPS

Common Abbreviations

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

μg	microgram
μm	micrometre
°Be	degrees Baumé (density)