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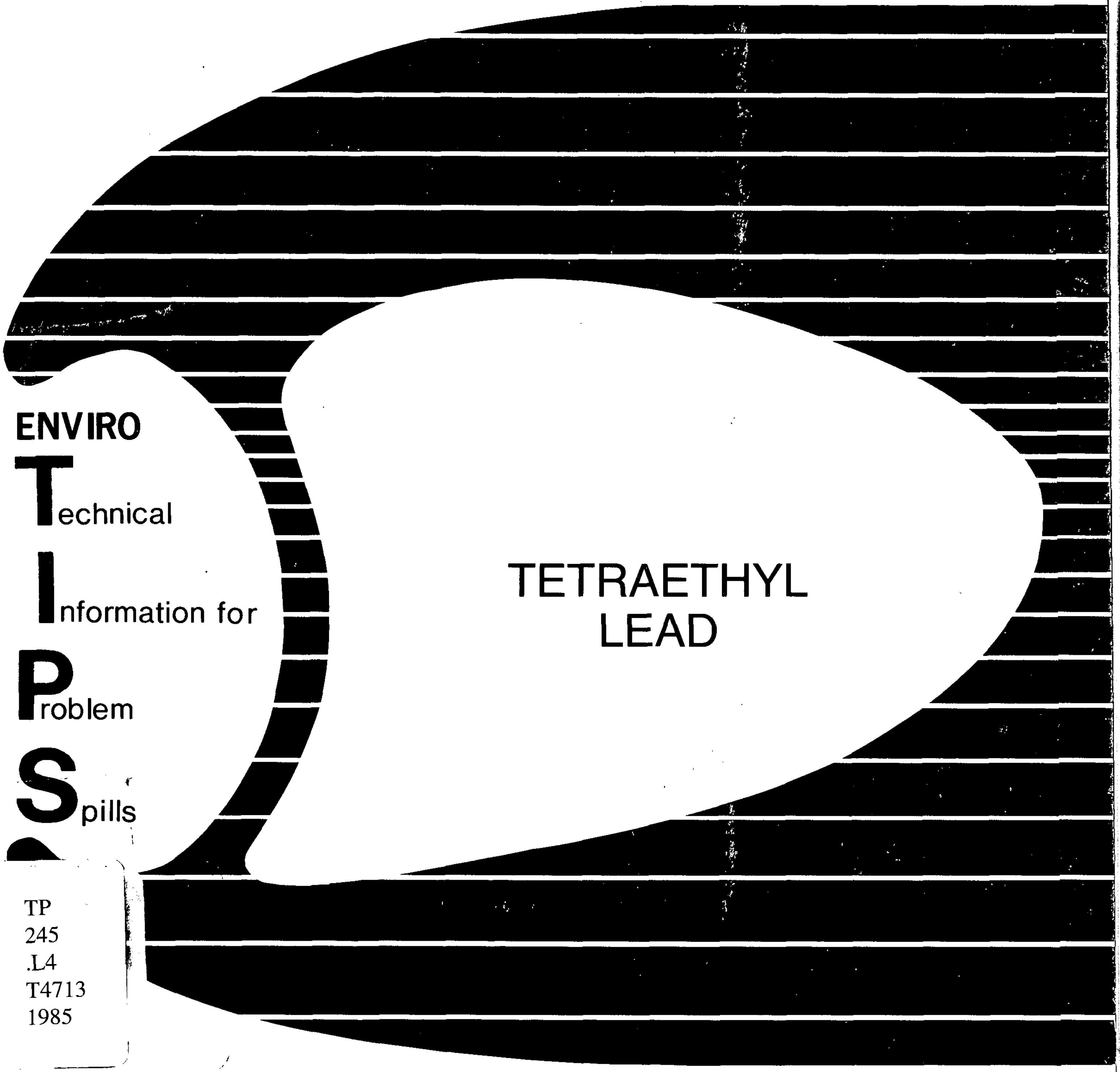

ENVIRO
Technical
Information for
Problem
Spills

TETRAETHYL LEAD

April 1985

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

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

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ENVIROTIPS - TETRAETHYL LEAD (English version only)

ERRATA

p.2, line 2	...Evacuate from downwind....not Evaluate
p.16, Figure 6	Max. Capacity 250L not 450L
p.33, Step 2:	...maximum radius calculated assuming a 2mm spill thickness.... not 2m
p.51, Section 6.2.1 line 4	...waters of hardness of less than 95mg/L.... not 95m/L

TETRAETHYL LEAD

12-12-96

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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Environmental Protection Programs Directorate
Environmental Protection Service
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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 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

TETRAETHYL LEAD ($(C_2H_5)_4Pb$)

Oily liquid; pure is colourless, but commercial mixtures may be dyed red, orange or blue.

SYNONYMS

TEL, Tetraethyl Lead Liquid, Tetraethyl-Plumbane, Motor Fuel Anti-Knock Compound

IDENTIFICATION NUMBERS

UN No. 1649; CAS No. 78-00-2; OHM-TADS No. 7216922; STCC No. 4921484

GRADES & PURITIES

Most tetraethyl lead is sold as motor anti-knock compound containing about 62 percent tetraethyl lead, 18 percent ethylene dibromide, 18 percent ethylene dichloride and about 2 percent dyes, solvents and antioxidants.

IMMEDIATE CONCERNS

Fire: Combustible. Vapours in fire contain lead compounds and are toxic.

Human Health: Very toxic. Poisonous by inhalation or skin absorption.

Environmental: Harmful to aquatic life in low concentrations.

PHYSICAL PROPERTY DATA

State: (15°C, 1 atm): liquid
Boiling Point: decomposes before boiling at about 200°C
Melting Point: -130.2°C
Flammability: combustible
Flash Point: 93°C (CC)
Density: 1.65 g/mL (20°C)
Solubility (in water): 0.8 to 2.0 mg/L (20°C)
Behaviour (in water): sinks with no reaction
Behaviour (in air): evaporates slowly

ENVIRONMENTAL CONCERNS

Tetraethyl lead is toxic to aquatic life at levels as low as 0.02 mg/L. It is more toxic to aquatic life, plants and mammals than most other forms of lead.

HUMAN HEALTH

TLV®: 0.1 mg/m^3 skin (as Pb)

IDLH: 3 ppm

Exposure Effects

Inhalation: Nose irritation, shivering, restlessness, delirium and convulsions.

Contact: (skin) Itching, inflammation, blisters; (eyes) irritation of eyes, inflammation. Extreme exposure could be fatal.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "POISON". Call fire department and notify manufacturer. Evaluate from downwind. Eliminate sources of ignition including traffic and equipment. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses. Cover pools of material with vapour suppressors (e.g., water) to minimize evaporation.

Fire Control

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

COUNTERMEASURES

Emergency Control Procedures in/on

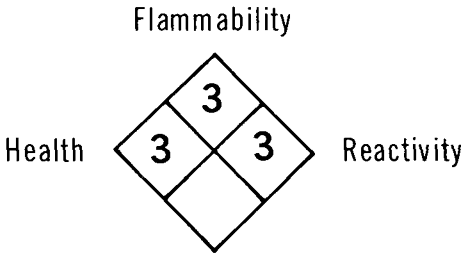
Soil: Construct barriers to contain spill or divert to impermeable holding area. Remove material by manual or mechanical means. Adsorb residual liquid on natural or synthetic sorbents.

Water: Contain by forming natural deep water pockets, sand bag barriers or natural barriers. Remove trapped material with suction hoses.

Air: Blanket spill pool with vapour suppressors (e.g., water) to minimize evaporation.

NAS HAZARD RATING

NFPA
HAZARD
CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Note: Many of the properties appearing below and throughout this manual refer to pure tetraethyl lead (TEL). The most common form is a mixture of TEL with ethylene dichloride and dibromide; this will be specifically noted by referring to this as TEL mix or its variants, TEL motor mix and TEL aviation mix.

Physical State Properties

Appearance	Colourless liquid when pure; may be dyed red, orange or blue
Usual shipping state	Liquid
Physical state at 15°C, 1 atm	Liquid
Melting point	-130.2°C (Bell 1978; Wilkinson 1982)
Boiling point	108.4°C (7 kPa) (Bell 1978) Decomposes before boiling at atmospheric pressure. Boiling point at atmospheric pressure estimated to be 199°C (Bell 1978)
Decomposition temperature	200°C (CRC 1980). Decomposition starts at room temperature and accelerates rapidly above 100°C (Wilkinson 1982)
Vapour pressure	0.036 kPa (20°C) (Barry 1973) 4.79 kPa (TEL motor mix at 20°C) (Ethyl MSDS 1972) 0.8 kPa (TEL aviation mix at 20°C) (Ethyl MSDS 1972)

Densities

Density	1.650 g/mL (20°C) (Wilkinson 1982)
Specific gravity	1.659 (11°C) (CRC 1980) 1.653 (20°C) (Ullmann 1975) 1.589 (TEL motor mix at 20°C) (Ethyl MSDS 1972) 1.744 (TEL aviation mix at 20°C) (Ethyl MSDS 1972)
Vapour density	8.6 (Verschueren 1984) 3.7 (Average components of TEL mix) (Ethyl MSDS 1972)

Fire Properties

Flammability	Flammable or combustible liquids (NFPA 1978)

Flash point	
CC	93°C (NFPA 1978)
OC	85°C (Bell 1978) >118°C (TEL mix) (Ethyl MSDS 1972)
Lower flammability limit	1.8 percent (v/v) (NFPA 1978)
Burning characteristics	Burns with an orange-coloured flame with a green margin (Merck 1976)
Heat of combustion	5920 kJ/mole (CHRIS 1978)
Combustion products	Carbon dioxide, water and lead; TEL mix can yield lead oxides, halides and oxyhalides (Bell 1978)
Decomposition temperature	200°C (CRC 1980)
Heat of decomposition	150 kJ/mole (Kirk-Othmer 1981)
Behaviour in a fire	Heating to decomposition could cause heat release and container explosion (NFPA 1978)

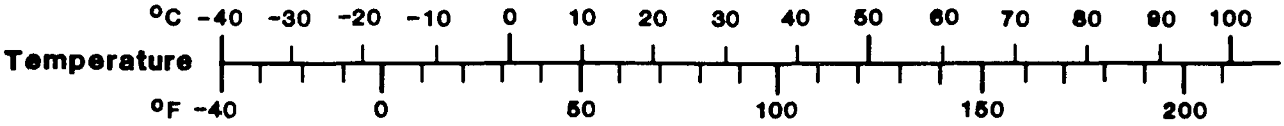
Other Properties

Molecular weight of pure substance	323.44 (CRC 1980)
Constituent components of typical commercial grade	Typically 61 percent tetraethyl lead (possibly in a mixture with tetramethyl lead) 18 percent (each) ethylene dibromide and dichloride (DuPont MSDS; Ethyl MSDS 1972)
Refractive index	1.5195 (30°C) (CRC 1980)
Viscosity	0.864 mPa•s (20°C) (Kirk-Othmer 1981)
Liquid interfacial tension with air	28.5 mN/m (25°C) (CHRIS 1978)
Liquid interfacial tension with water (est.)	40 mN/m (20°C) (CHRIS 1978)
Latent heat of fusion	8.80 kJ/mole (at melting point) (Kirk-Othmer 1981)
Latent heat of vaporization	54.2 kJ/mole (CRC 1980) 53.34 kJ/mole (Ullmann 1975)
Heat of formation	53.1 kJ/mole (25°C) (Sussex 1977)
Ionization potential	11.1 eV (Rosenstock 1977)
Heat capacity constant pressure (Cp)	141-262 J/(mole•°C) (Kirk-Othmer 1981)
Critical temperature	380°C (CND 1972)
Critical pressure	2100 kPa (CND 1972)

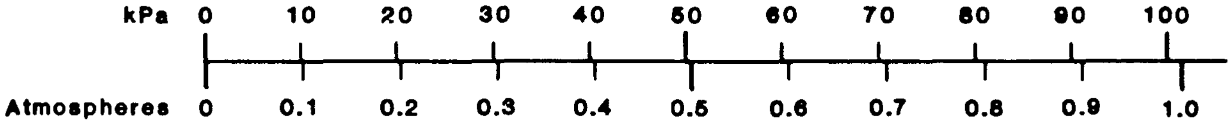
Solubility

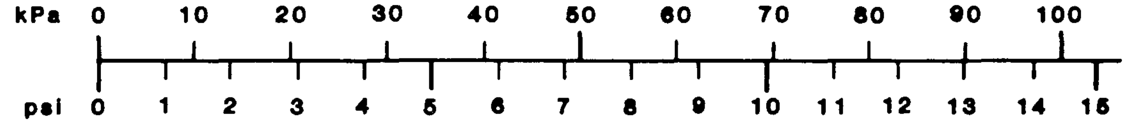
In water	Distilled water: 0.8 mg/L (Pb) (20°C) (Grove 1980) Seawater: 2.0 mg/L (Pb) (20°C) (Grove 1980)
In other common materials	Soluble in benzene, ethanol and diethyl ether (CRC 1980)

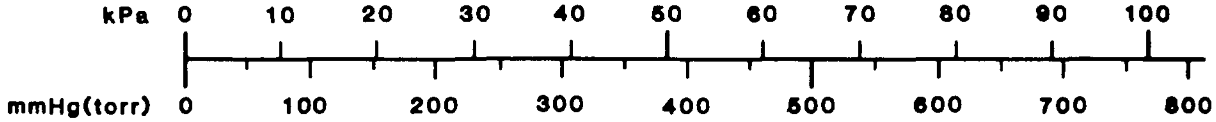
CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa







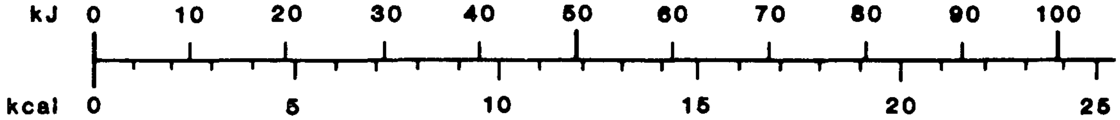
Viscosity

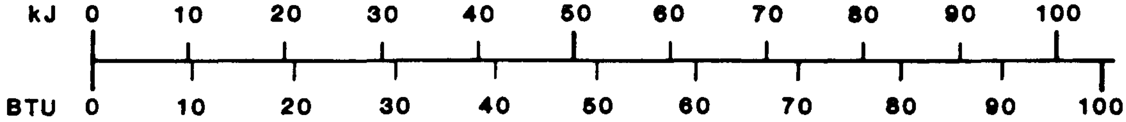
Dynamic 1 Pa·s = 1 000 centipoise (cP)

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

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

Energy (heat) 1 kJ = 1 000 J





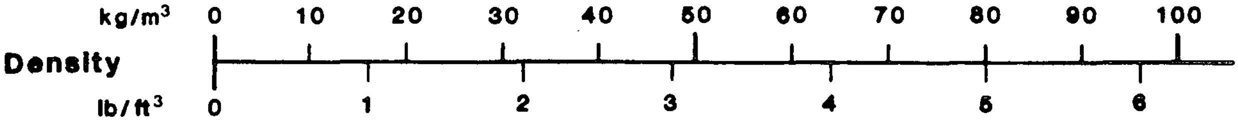


FIGURE 1

TETRAETHYL LEAD

VAPOUR PRESSURE VS TEMPERATURE

Reference: CHRIS 1978

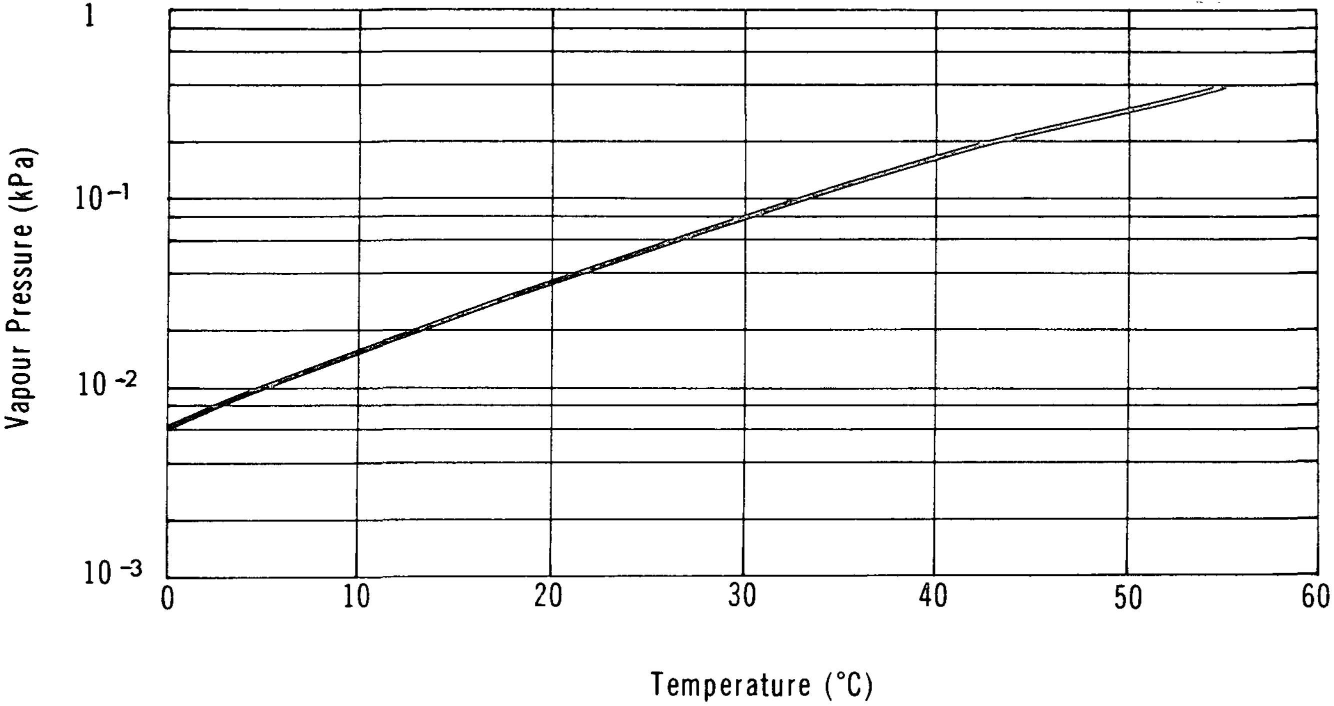


FIGURE 2

TETRAETHYL LEAD

LIQUID DENSITY VS TEMPERATURE

Reference: CHRIS 1978

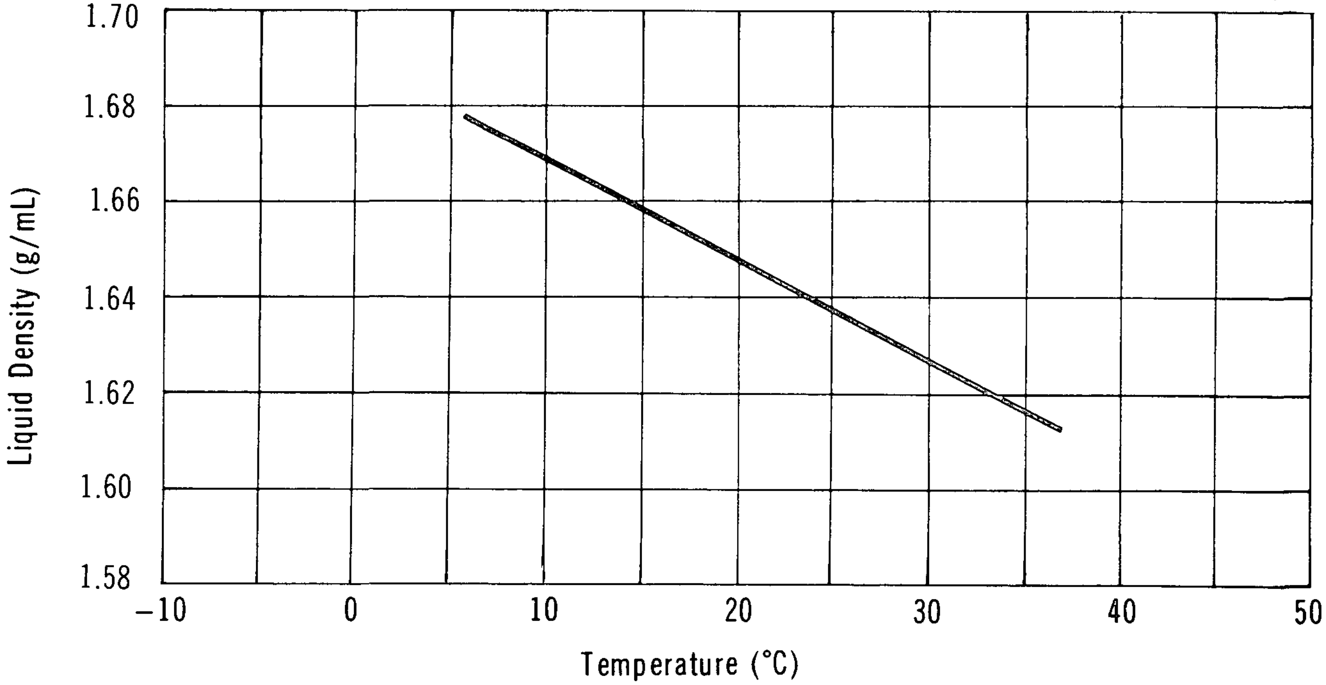


FIGURE 3

TETRAETHYL LEAD

LIQUID VISCOSITY VS TEMPERATURE

Reference: CHRIS 1978

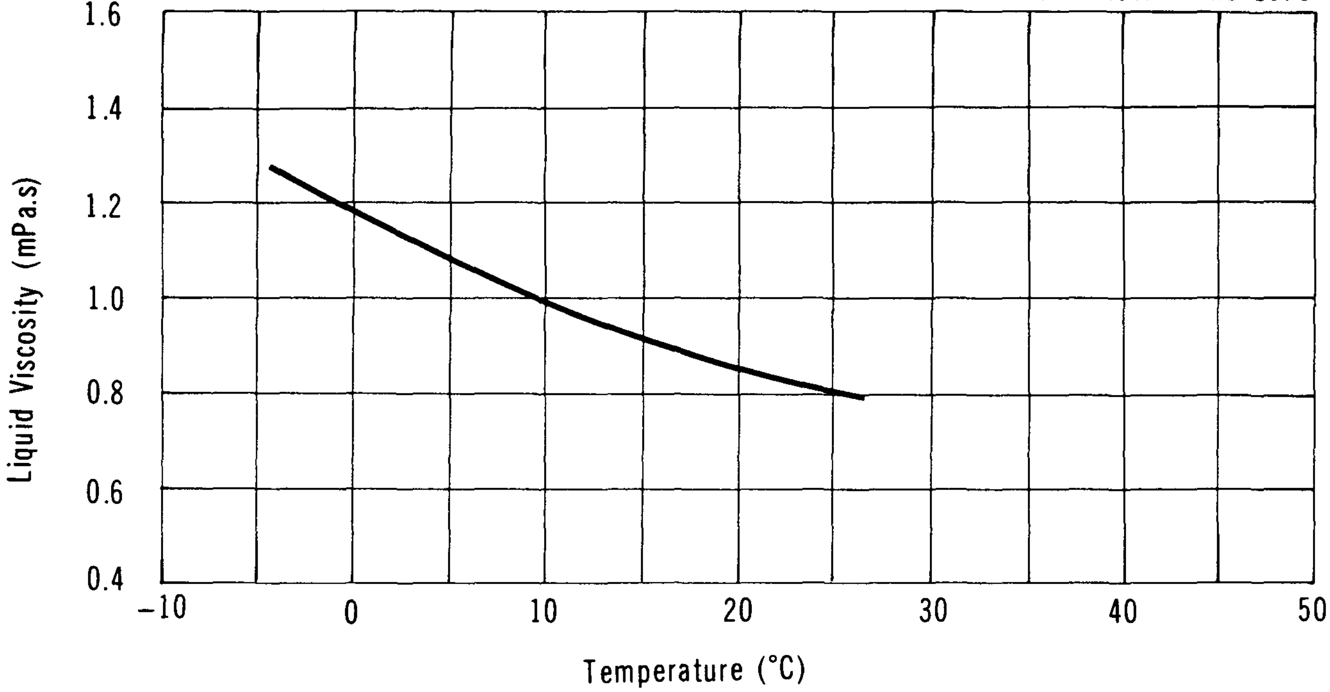
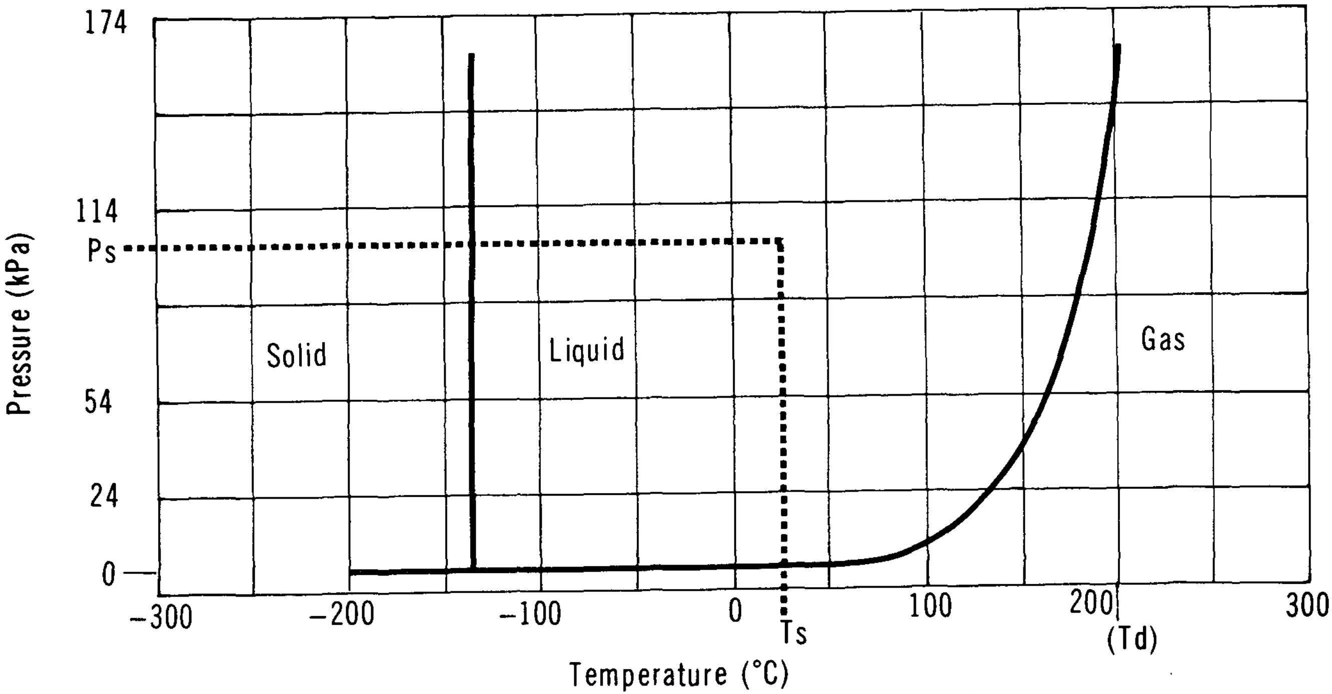


FIGURE 4

TETRAETHYL LEAD

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities

Tetraethyl lead (TEL) is sold in a number of grades and purities. The pure grade, which is rarely sold, is available in litre cans which contain a minimum of 99.0 percent by weight pure tetraethyl lead (Ethyl Corp.). The most commonly available grade of tetraethyl lead is the TEL motor mix; the TEL aviation mix is less common. The concentrations of the product and its additives are tabulated below (Du Pont MSDS):

		Concentration (percent by weight)		
Grade	TEL	Ethylene Dibromide	Ethylene Dichloride	Dye, Solvents, Antioxidants
TEL Motor Mix	61.5	17.9	18.8	1.8
TEL Aviation Mix	61.5	35.7	-	2.8

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

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

Du Pont Canada
555 Dorchester Blvd. West
P.O. Box 6600
Montreal, Quebec
H3C 2V1
(514) 861-3861

Ethyl Canada Inc.
48 St Clair Avenue West
Toronto, Ontario
M4V 1M7
(519) 962-1611

3.3 **Major Transportation Routes** (Corpus 1983; Du Pont 1982)

Current Canadian production of tetraethyl lead is in Ontario, at Maitland and Sarnia. The product is sold directly to oil refineries across Canada. It is primarily shipped by tank car and tank truck.

3.4 Production Levels (Corpus 1983)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1982)
Du Pont Canada, Maitland, Ont.		15
Ethyl Corp. of Canada, Sarnia, Ont.		22
	TOTAL	37
Domestic Production (1982)		13
Imports (1982)		-
	TOTAL SUPPLY	13

3.5 Manufacture of Tetraethyl Lead (FKC 1975)

Tetraethyl lead (TEL) is produced by ethylation of a lead-sodium alloy according to the following reaction:

$$4NaPb + 4C_2H_5Cl \rightarrow (C_2H_5)_4Pb + 3Pb + 4NaCl$$

It may be catalyzed by a variety of carbonyl, hydroxyl and amine compounds. The alloy is introduced to the reactor with excess ethyl chloride at reaction conditions of 1.6 to 2.1 MPa (230-300 psi) and 110-150°C. Under these conditions, the reaction is complete in several minutes; the reaction mass is then steam-distilled to remove TEL and ethyl chloride. The remaining solid mass, lead (three quarters of the lead required is unconsumed) and sodium chloride from the reaction, is water-washed to remove the salt; the lead is then dried and recycled to make more lead-sodium alloy. The excess ethyl chloride is separated from the TEL, purified, and recycled; the TEL is purified by treatment with dilute oxidizing agents. Salt and hydrocarbons from Wurtz side reactions are byproducts of this process.

3.6 Major Uses in Canada (Corpus 1983)

Tetraethyl lead is used mainly in gasoline as a motor anti-knock additive. In 1983, this use accounted for all of domestic production.

3.7 Major Buyers in Canada (Corpus 1983)

Chevron Standard, Vancouver, B.C.
Golden Eagle, St. Romuald, Que.; Holyrood, Nfld.
Gulf Canada, Toronto, Ont.

Husky Oil, Lloydminster, Alta.
Imperial Oil, Sarnia, Ont.; Edmonton, Alta.; Dartmouth, N.S.
Irving Oil, St. John, N.B.
PetroCanada, Montreal, Que.; Trafalgar, Ont.
Shell Canada, Sarnia, Ont.; Edmonton, Alta.
Sunoco, Sarnia, Ont.
Texaco Canada, Don Mills, Ont.; Dartmouth, N.S.; Edmonton, Alta.
Ultramar, St. Romuald, Que.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 **Bulk Shipment.** Tetraethyl lead is shipped bulk in specially designed railway tank cars, tank motor vehicles and portable tanks.

4.1.1.1 **Railway tank cars.** Railway tank cars used in the transportation of tetraethyl lead are of type 105A300. Table 2 describes this classification (RTDCR 1974; TCM 1979). Figure 5 and Table 3 provide additional details on this type of car. The tank cars used are smaller than for most other commodities, primarily because of the relative volume used at one time. The most common sizes are 12 000 L (2600 gal.) and 24 000 L (5300 gal.) (CCPA 1983).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
105A300W	Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Bottom outlet or washout prohibited. Test pressure 2070 kPa (300 psi).

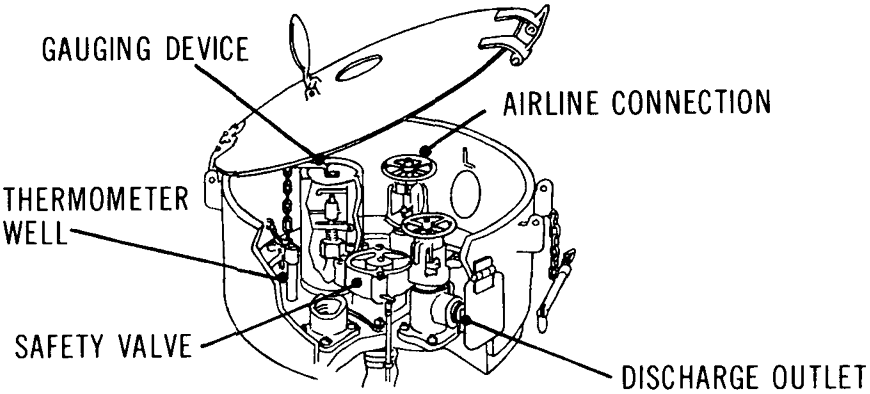
* Canadian Transport Commission and Department of Transportation (U.S.)

Rail cars are equipped only for top unloading by pump or compressed air. Tetraethyl lead is withdrawn through an eduction tube which extends from the bottom of the tank to the top operating platform where it terminates at an unloading connection, usually a 51 mm (2 in.) valve (TCM 1979).

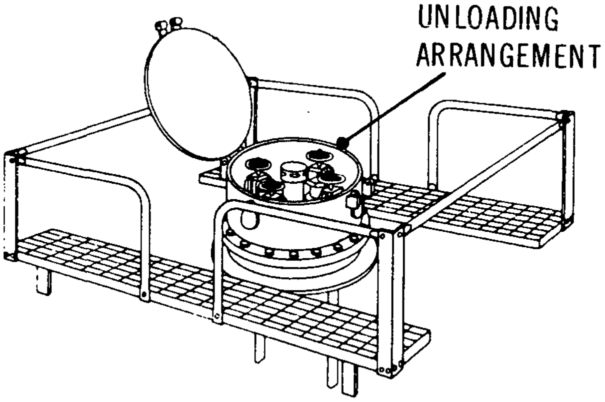
Air pressure of 138 kPa (20 psi) is applied through an air connection valve, usually of 25 mm (1 in.) size. Tanks are constructed of nickel alloy plate or steel plate A283, Grade C, with nickel lining. Outage must be sufficient to prevent the tank from becoming liquid full at 55°C (TDGC 1980). Railway tankers must have an approved pressure relief valve or a frangible disc preceding a spring-loaded valve. The space between the disc and valve should be provided with a pressure gauge. The maximum pressure allowable for CTC/DOT 105A300W tankers is 1380 kPa (200 psi) (RTDCR 1974).

RAILWAY TANK CAR CLASS 105A300W

Reference: TCM 1979; RTDCR 1974



Detail of top unloading arrangement



Detail of loading platform

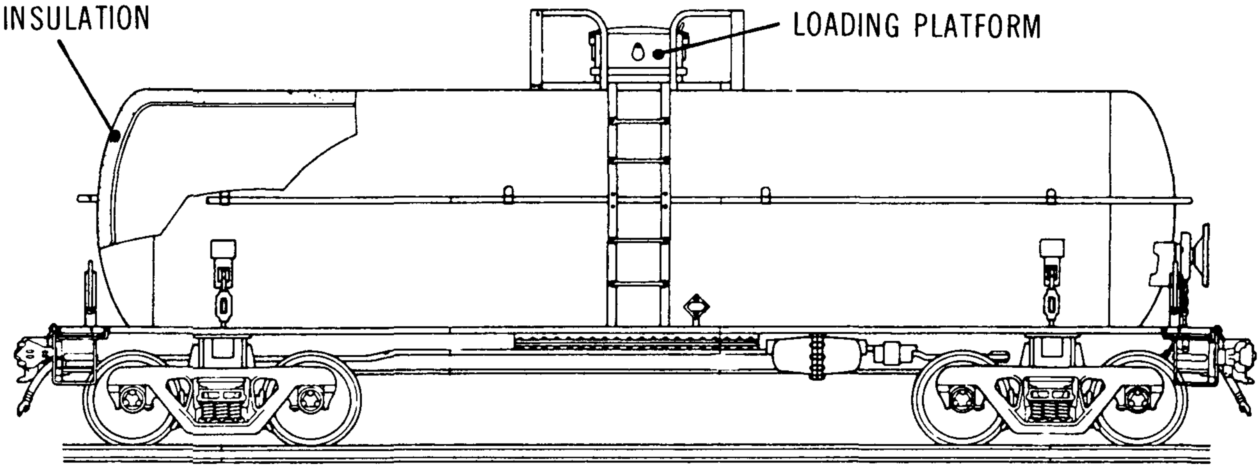


Illustration of tank car layout

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

	Tank Car Size (Imp. Gal.)			
Description	2600		5300	
Overall				
Nominal capacity	12 000 L	(2600 gal.)	24 000 L	(5300 gal.)
Car weight - empty	28 500 kg	(62 800 lb.)	40 800 kg	(90 000 lb.)
Car weight - max.	80 300 kg	(177 000 lb.)	83 500 kg	(184 000 lb.)
Tank				
Material	Steel		Steel	
Thickness	17.5 mm	(11/16 in.)	17.5 mm	(11/16 in.)
Inside diameter	1.5 m	(60 in.)	2.0 m	(77 in.)
Test pressure	2070 kPa	(300 psi)	2070 kPa	(300 psi)
Burst pressure	51 700 kPa	(750 psi)	51 700 kPa	(750 psi)
Approximate Dimensions				
Coupled length	11 m	(37 ft.)	12 m	(40 ft.)
Length over strikers	10 m	(35 ft.)	11 m	(37 ft.)
Length of truck centres	7 m	(24 ft.)	8 m	(27 ft.)
Height to top of grating	3 m	(11 ft.)	3 m	(11 ft.)
Overall height	4 m	(12 ft.)	4 m	(14 ft.)
Overall width	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2 to 3 m	(7 to 10 ft.)	2 to 3 m	(7 to 10 ft.)
Width of grating	1.5 to 2 m	(5 to 6 ft.)	1.5 to 2 m	(5 to 6 ft.)
Loading/Unloading Fixtures				
Unloading connection	51 mm (2 in.) via valve and 76 mm (3 in.) check valve; 6 mm (1/4 in.) outlet.			
Gauging Device	Float-type gauging device and thermometer well.			
Safety Devices	Safety relief valve set at 1550 kPa (225 psi).			
Insulation	51 to 152 mm (2 to 6 in.) fibreglass insulation.			

4.1.1.2 Tank motor vehicles. Truck motor vehicles or highway tankers are used less frequently than railway tank cars. These tankers must conform to Transport Canada Specification TC331 which states that these cargo tanks must be of seamless or welded steel construction, or a combination of both, and must be designed and constructed in accordance with the ASME Code. Post-weld heat treatment must be as prescribed in the ASME Code (TDGC 1980).

Safety relief valves are to be installed in such a manner as to have direct communication with the vapour space of the tank. They are similar in design and construction to those described for rail cars.

4.1.1.3 Portable tanks. Portable tanks have been used to transport small volumes of tetraethyl lead. The capacities and weights of tanks vary depending on requirements of the user. Unloading fittings and methods are similar to those discussed for railway tank cars and highway tankers. Portable tanks must conform to Specification TC51. Table 4 describes this specification (TDGC 1980).

TABLE 4 PORTABLE TANK SPECIFICATIONS

TC* Specification Number	Description
TC51	Seamless or welded steel construction or combination of both. Minimum tank water capacity of 455 kg (1000 lb.). Minimum shell and head thickness 5 mm (3/16 in.). Design and construct in accordance with ASME Code. Fusion-welded tank and permanent attachments to be postweld heat-treated and radiographed to provide highest joint efficiency provided by ASME Code. Minimum design pressure 690 kPa (100 psi). Maximum design pressure 3450 kPa (500 psi).

*Transport Canada

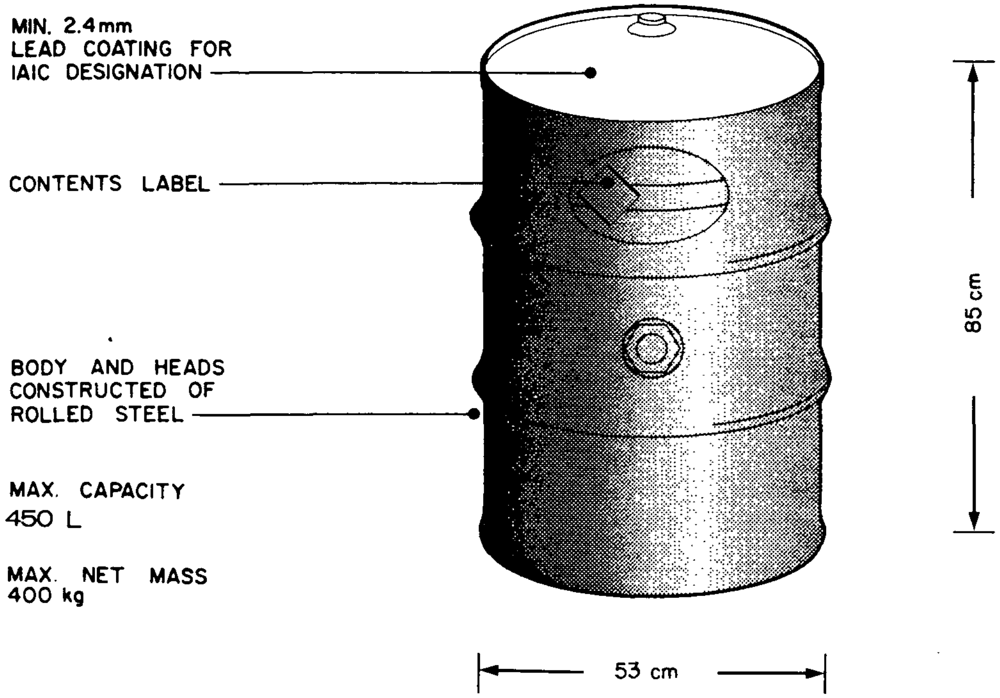
4.1.2 Packaging. Tetraethyl lead may be packaged in drums for transportation. Steel drums of Specification 5 or 5A may be used (RTDCR 1974). A typical steel drum is illustrated in Figure 6.

FIGURE 6

TETRAETHYL LEAD

TYPICAL DRUM CONTAINER

Typical steel drum



In addition, glass carboys (boxed or in expanded polyethylene) or wooden boxes wirebound with liner may be used (TDGC 1980). The maximum capacity of carboys is 49.2 L (10.8 gal.); the maximum gross mass of wirebound wooden boxes is 181 kg (399 lb.) (TDGC 1980).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars and Tank Motor Vehicles. Prior to off-loading, certain precautions must be taken (TCM 1979):

- The vented 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 employed, and caution placards displayed.
- A safe operating platform must be provided at the unloading point.

Proceed with top off-loading by air as follows (TCM 1979):

- After removing the protective housing from the air inlet and discharge line at the top of the car, 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 138 kPa (20 psi) for unloading. A safety relief valve must be installed in the air line to release at 159 kPa (23 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.

For off-loading by pump, connect the pump suction to the 51 mm (2 in.) outlet connection. The tank vent valve should be opened to prevent a vacuum from occurring in the tank.

4.2.2 Specifications and Materials for Off-loading Equipment. 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 fittings are recommended at normal temperatures and pressures. Flanged joints (e.g., "ammonia" type flanges) should be used and these should be welded. Stress relief at the weld will also lengthen the serviceability of the pipe. After installation, the pipeline should be tested with water at pressures from 345 to 518 kPa (50-75 psi) and all leaks carefully stopped.

The unloading line is usually 51 mm (2 in.) in diameter but process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining. Specially designed hose or solid pipe with swivel joints may be used for the flexible sections of the unloading line (GF). Either the ball bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance.

Cast iron or cast steel diaphragm valves lined with chlorinated polyether will serve adequately (DPLV 1972). Viton can be used satisfactorily as a gasket material at normal temperatures (Dow PPS 1972). A single-suction, sealless magnetic drive centrifugal pump with wet end material of 316 stainless steel is recommended for pumping. Welded steel storage tanks are commonly used. A resistant lining or nickel-cladding inside the tank may be used.

4.3 Compatibility with Materials of Construction

The compatibility of tetraethyl lead 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 as follows:

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.

Note: A number of plastics, although shown as "conditional" in the following table, are "recommended" by a number of manufacturers but are not recommended in this manual for planned and long-term service. Most plastics will absorb TEL to some extent and thus will deteriorate; also, for short-term service, they would become contaminated with TEL and would thus have to be disposed of.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings		23		PVC II (DPPED 1967)	
		24		PVC I (MWPP 1978)	
		60		PVC I (DPPED 1967)	
		107		Chlorinated Polyether (DCRG 1980)	
		135		PVDF (DCRG 1980)	
	Most	Most	CS Stainless Steel		ABS PE (MWPP 1978)
2. Pumps			Bronze Fitted or All Iron (HIS 1969)		
3. Others	Technically Pure	20		uPVC, PE PP, POM NBR, IIR EPDM, CR FPM, CSM (GF)	NR (GF)

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

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
3. Others (Cont'd)		22		PVC, CPVC (TPS 1978)	
		121		PVDF (TPS 1978)	
	Most	Most		CS Stainless Steel	

TABLE 6 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Aluminum
	Bronze
	Carbon Steel
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene) Rubber
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Iron
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
	Nickel
PE	Polyethylene
PP	Polypropylene

TABLE 6 MATERIALS OF CONSTRUCTION (Cont'd)

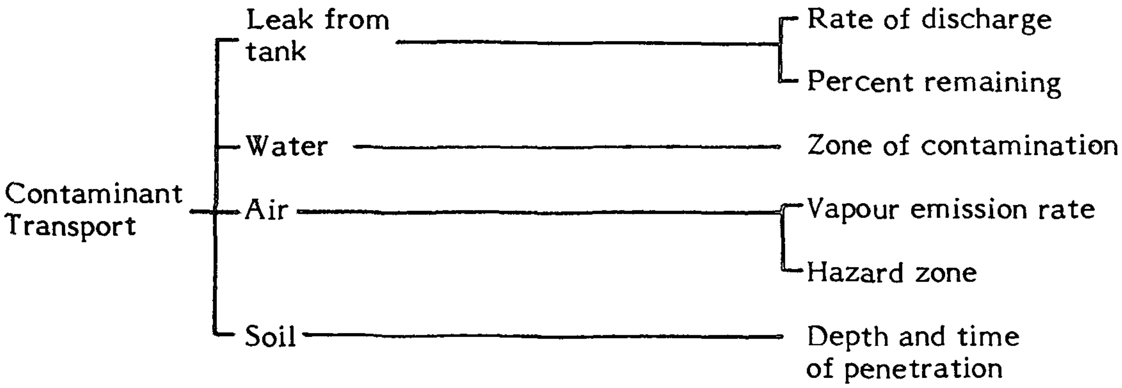
Abbreviation	Material of Construction
POM	Polyoxymethylene
PVC (followed by grade)	Polyvinyl Chloride
PVDF	Polyvinylidene Fluoride
uPVC	Unplasticized Polyvinyl Chloride

5 CONTAMINANT TRANSPORT

5.1 General Summary

Tetraethyl lead, when spilled in water, will sink and spread on the stream bottom. When spilled on soil, it 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 will be an environmental concern. Since tetraethyl lead is moderately volatile, the vapour released from a liquid pool on the ground surface is a potential environmental hazard.

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



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. Tetraethyl lead is commonly transported in railway tank cars as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size has been chosen throughout the EnviroTIPS series for development of the leak nomograms. This allows for comparisons among the various chemicals. The standard tank car is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L. It must be noted that the two most commonly used tank cars are 15 and 30 percent of this size; for a first approximation, the values which will be calculated can be scaled down using these percentages.

If a tank car loaded with tetraethyl lead 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 tetraethyl lead and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

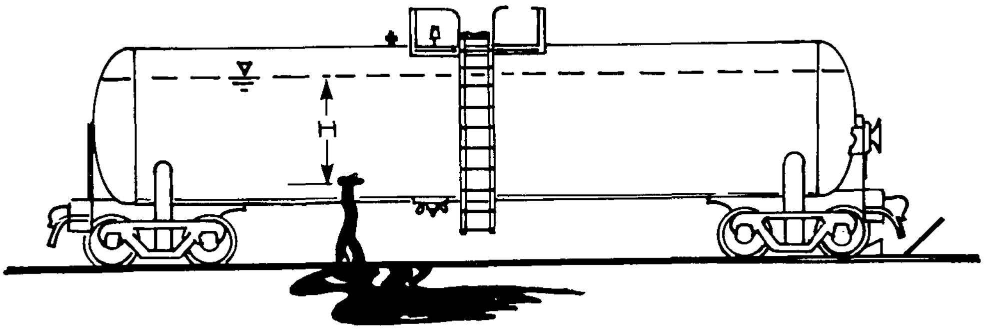


FIGURE 7 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

5.2.2 Nomograms.

5.2.2.1 Figure 8: Percent remaining versus time. Figure 8 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car is assumed to be initially full (at t=0) with a volume of about 80 000 L of tetraethyl lead. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

5.2.2.2 Figure 9: Discharge rate versus time. Figure 9 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture for a number of equivalent hole diameters.

FIGURE 8

TETRAETHYL LEAD

PERCENT REMAINING VS TIME

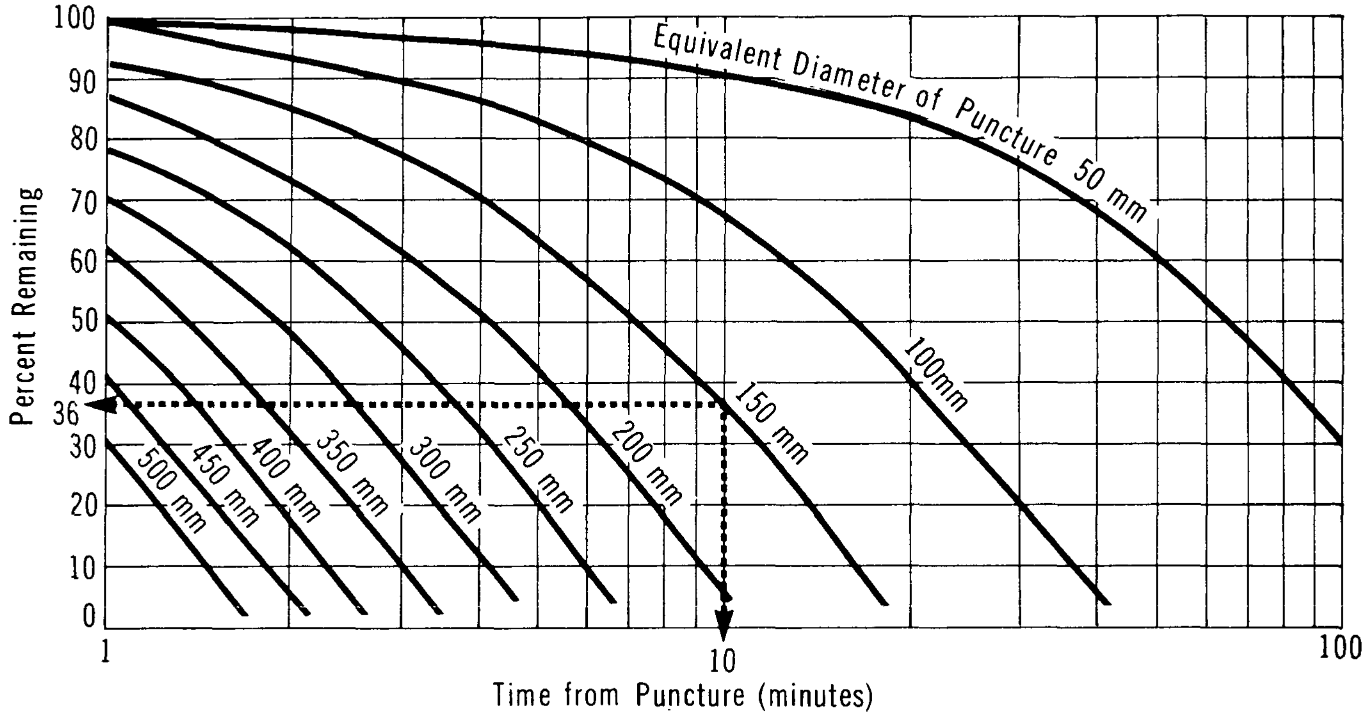
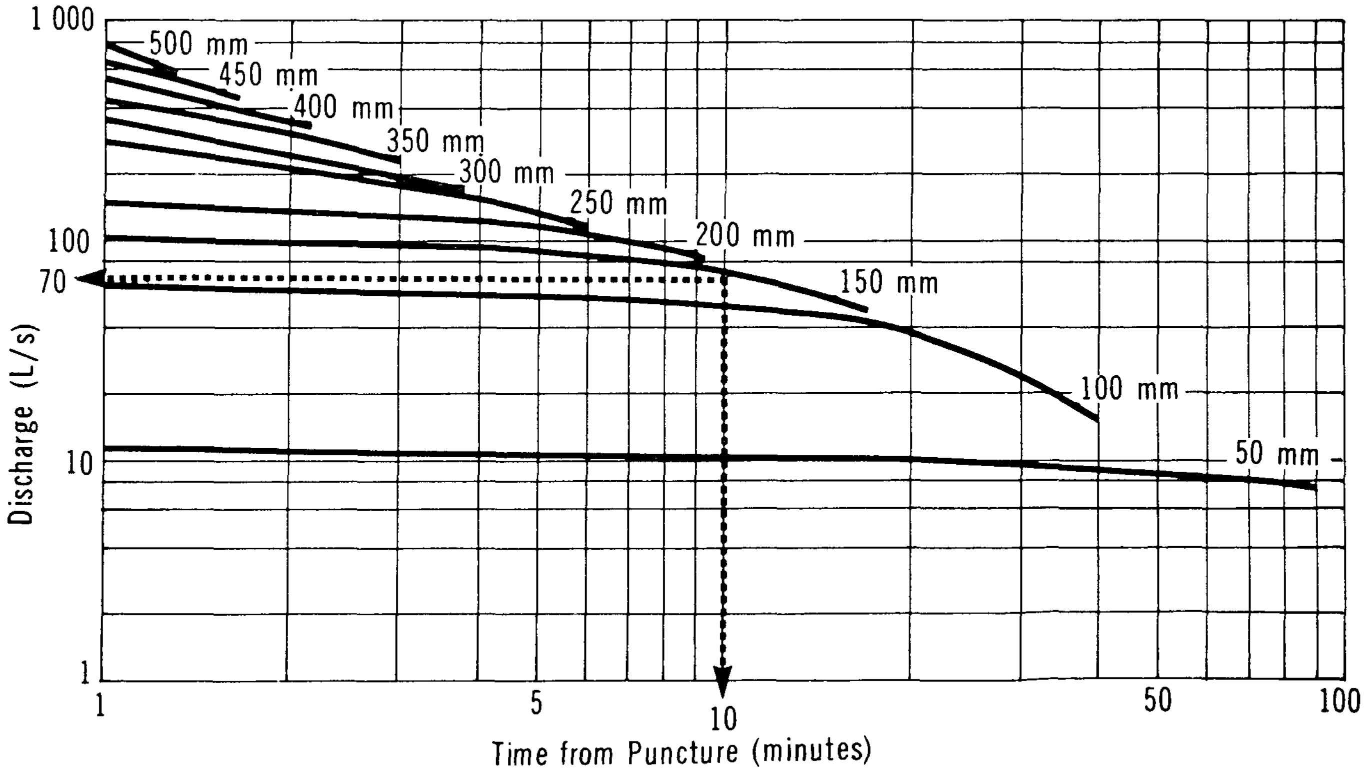


FIGURE 9

TETRAETHYL LEAD

DISCHARGE RATE VS TIME



5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with tetraethyl lead has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 8
- With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28 800 L
- If the 24 000 L tank car was involved, a first approximation would be that 36 percent, or 36/100 x 24 000 = 8600 L remains

ii) Problem B

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

Solution to Problem B

- Use Figure 9
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s
- With a tank car of 24 000 L, a first approximation would be that the discharge rate would be 36/100 x 70 = 25 L/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since tetraethyl lead has a moderate volatility, direct venting of the vapour to the atmosphere from a hole in a punctured vessel does not constitute a significant hazard downwind. Only vapour released from a liquid pool spilled on a ground surface is treated here. Spills on water are modelled on the basis that tetraethyl lead is both insoluble in and much denser than water.

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

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

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

Figure 12:	vapour emission rate from a liquid pool as a function of maximum pool radius
Table 7:	weather conditions
Figure 13:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 8:	maximum plume hazard half-widths
Figure 14:	vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 11 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" and "equivalent pool radius" are contained in Sections 5.2 and 5.4, respectively. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 12: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for tetraethyl lead has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for tetraethyl lead at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 0.032 g/(m^{2}s). Evaporation rates at other temperatures have been calculated using the evaporation rate equation which at a given wind speed is dependent on ambient temperature and the vapour pressure (CHRIS 1978) of tetraethyl lead at that temperature. For example, evaporation rates of 0.006 g/(m^{2}s) at 0°C and 0.06 g/(m^{2}s) at 30°C were calculated for a wind speed of 4.5 m/s.

Use: For a pool of tetraethyl lead of known radius, the rate (Q) at which tetraethyl lead vapour is released to the atmosphere at a given temperature can then be estimated from Figure 12. The solid portions of the curves represent spills of 1 to 130 tonnes, the latter representing about one standard 80 000 L rail car load of tetraethyl

FIGURE 10

TETRAETHYL LEAD

CONTAMINANT PLUME

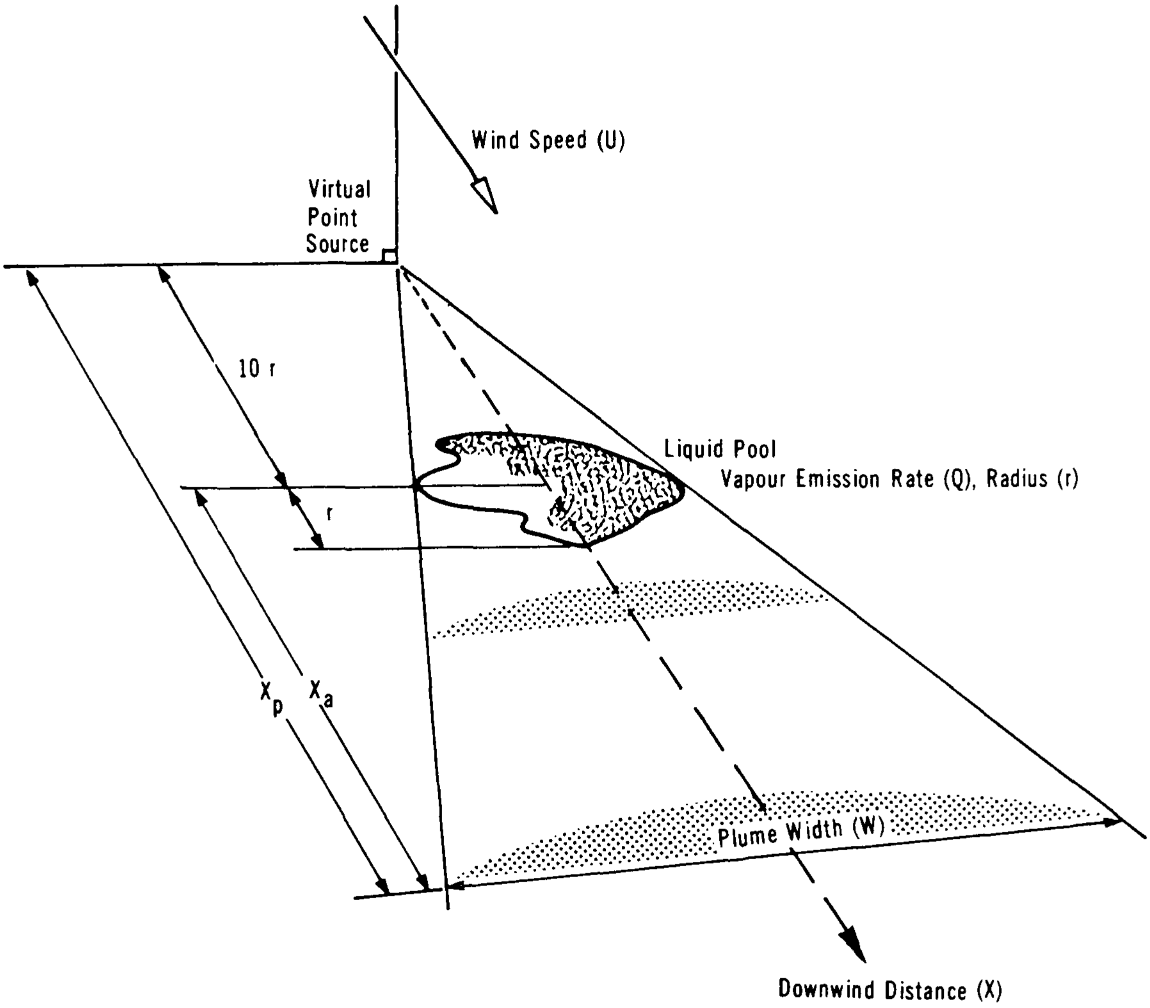
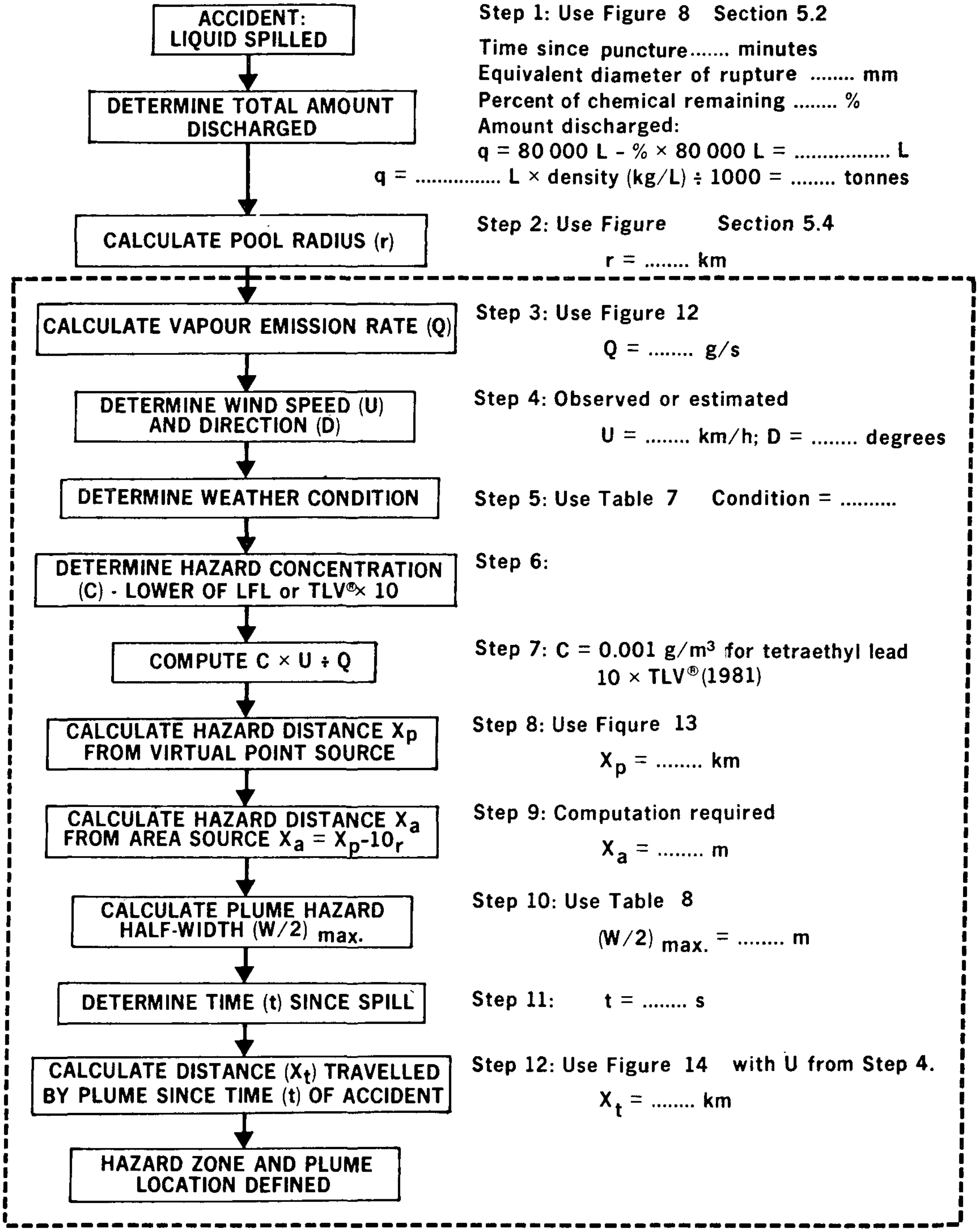


FIGURE 11

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE



Step 1: Use Figure 8 Section 5.2
Time since puncture....... minutes
Equivalent diameter of rupture .... mm
Percent of chemical remaining .... %
Amount discharged:
q = 80 000 L - % × 80 000 L = ... L
q = ... L × density (kg/L) ÷ 1000 = ... tonnes

Step 2: Use Figure Section 5.4
r = ... km

Step 3: Use Figure 12
Q = ... g/s

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

Step 5: Use Table 7 Condition = ...

Step 6:

Step 7: C = 0.001 g/m^3 for tetraethyl lead
10 × TLV®(1981)

Step 8: Use Fiqure 13
X_p = ... km

Step 9: Computation required
X_a = ... m

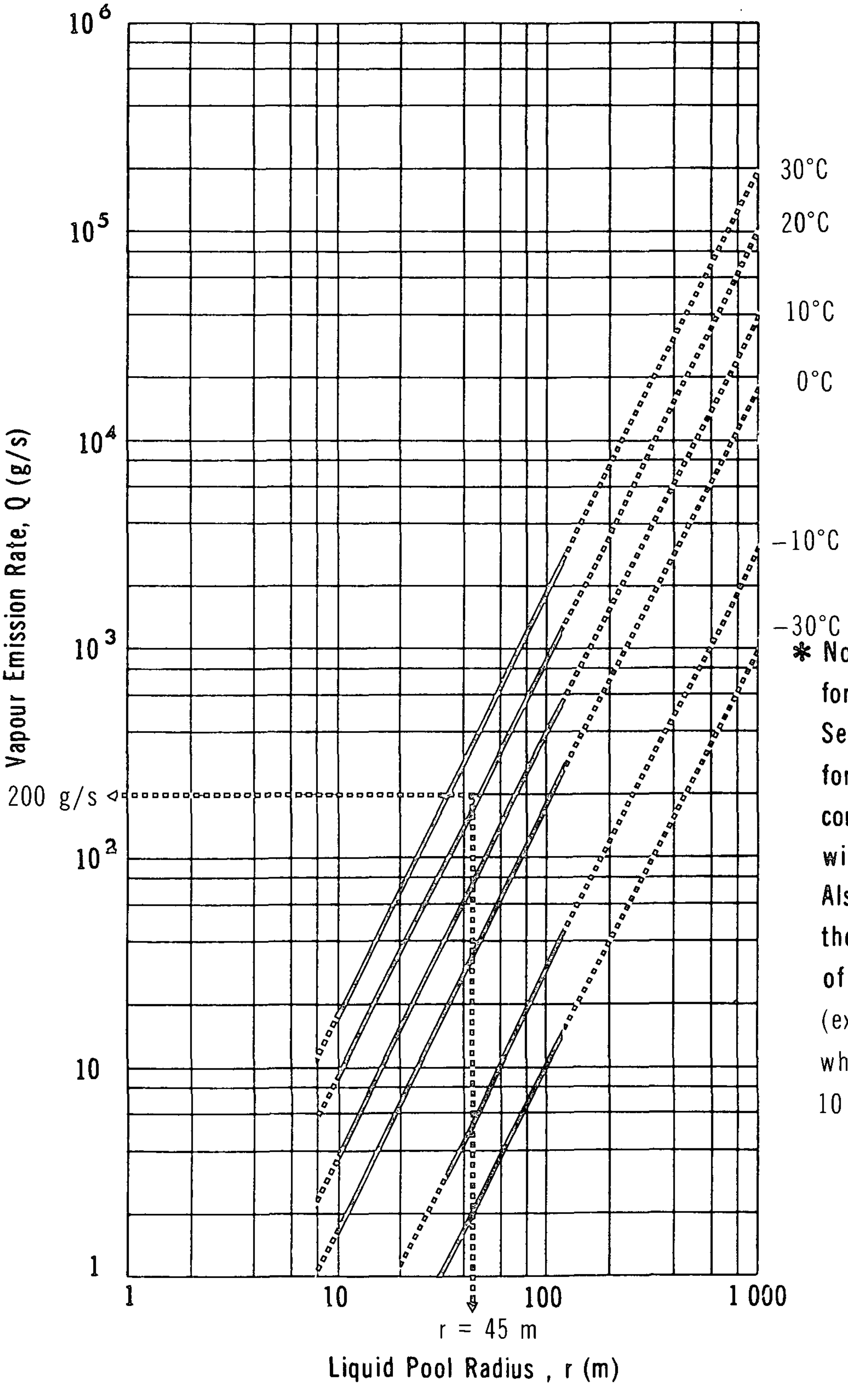
Step 10: Use Table 8
$(W/2)_{max.}$ = ... m

Step 11: t = ... s

Step 12: Use Figure 14 with U from Step 4.
X_t = ... km

FIGURE 12

VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES



✱ Note: Nomogram applies for wind speed of 4.5 m/s. See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 1 to 130 tonnes. (except −30°C and −10°C, where lower limit is 10 tonnes) lead. It should be noted that Figure 12 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of tetraethyl lead vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

It should also be noted that the determination of the emission rate is based on an arbitrary spill radius on flat land. The spill radius for any given spill amount was calculated assuming a 2 mm depth of spill value and assuming symmetrical spreading of the spilled liquid. The resultant spill radius is considered to provide the maximum value, since the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous) would likely show a smaller observed spill radius.

5.3.2.2 Figure 13: Normalized vapour concentration versus downwind distance. Figure 13 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 13, the weather condition must be determined from Table 7.

TABLE 7 WEATHER CONDITIONS

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

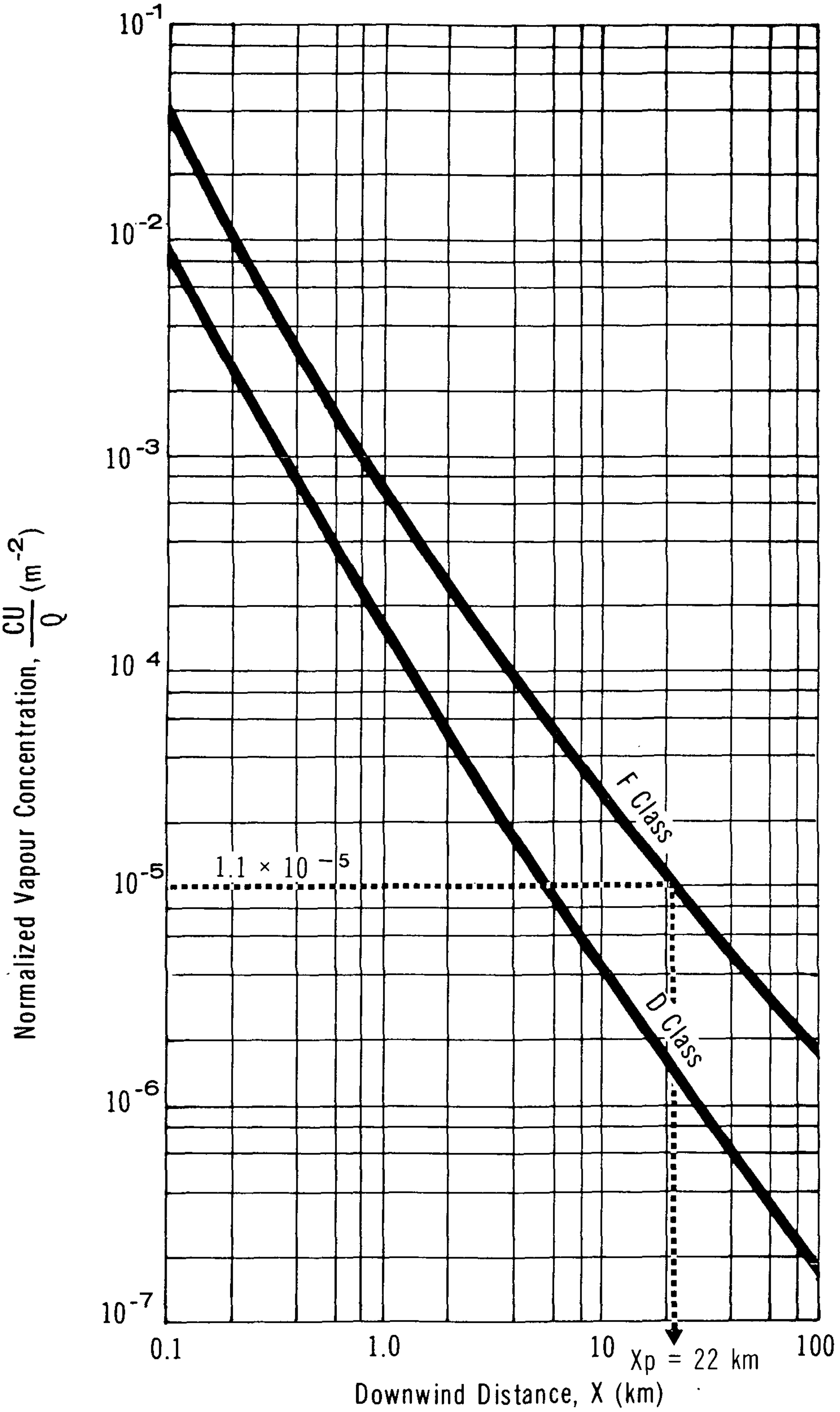
Use: The maximum hazard distance, X_p, downwind of the spill can be calculated from Figure 13 knowing:

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

FIGURE 13

TETRAETHYL LEAD

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



- 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 an inflammable vapour will be 10 x TLV®. Note that the TLV® for tetraethyl lead is provided only in g/m^3 and is not pertinent in ppm. Therefore, a conversion nomogram (from ppm to g/m^3) is not provided.

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 in the short-term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure and use of this value as the hazard limit would result in unrealistically large hazard zones.

5.3.2.3 **Table 8: Maximum plume hazard half-widths.** This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the tetraethyl lead Threshold Limit Value (TLV®) of 0.0001 g/m^3, or 0.001 g/m^3. The maximum plume hazard half-width represents the maximum half-width of the tetraethyl lead vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 8 is therefore only applicable for a tetraethyl lead hazard concentration limit of 10 x TLV®, or 0.001 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 15 to 7000 g/s, corresponding to tetraethyl lead spills in the range of about 2 to 700 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spills, the mass spilled would be 130 600 kg, or approximately 131 tonnes. Therefore, under class D of Table 8, data are provided for up to 5 times a standard rail car load, or up to 16 times a 24 000 L tank car.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 1.5 to 1650 g/s, corresponding to tetraethyl lead spills in the range of about 0.2 to 65 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to half a standard rail car load or 1-2/3 of a 24 000 L tank car.

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

Weather Condition D			Weather Condition F		
Q/U (g/m)	$(W/2)_{max}$ (m)		Q/U (g/m)	$(W/2)_{max}$ (m)	
7000	3430	(99.5 km)*	650	1520	(99.5 km)*
6000	3115		600	1430	
5000	2785		500	1250	
4000	2425		400	1060	
3000	2030		300	850	
2500	1815		250	745	
2000	1580		200	630	
1500	1320		150	510	
1000	1030	Q/U = 95 →	100	375	→ $(W/2)_{max}$ = 375 m
750	860		75	310	
500	670		50	240	
400	585		25	155	
300	500		10	85	
200	395		5	55	
100	260		2.5	35	
75	220		1	25	
50	175		0.5	15	
25	115				
10	70				
5	50				
2.5	35				
1	20				
0.5	15				

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

Example: A spill releasing tetraethyl lead vapour at the rate of Q = 200 g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 95 g/m which results in a maximum plume hazard half-width $(W/2)_{max}$ = 375 m.

Note: Above table is valid only for a tetraethyl lead concentration of 10 x TLV®, or 0.001 g/m^3.

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

5.3.2.4 Figure 14: Plume travel time versus travel distance. Figure 14 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

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

5.3.3 Sample Calculation.

The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid tetraethyl lead. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill radius) in a particular spill situation if possible.

Problem:

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

Solution:

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

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

- Use the observed (measured) pool radius if possible. If not, use the maximum radius calculated assuming a 2 m spill thickness
- Radius (r) = 45 m ÷ 1000 = 0.045 km

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

- From Figure 12, for r = 45 m and T = 20°C, Q = 200 g/s

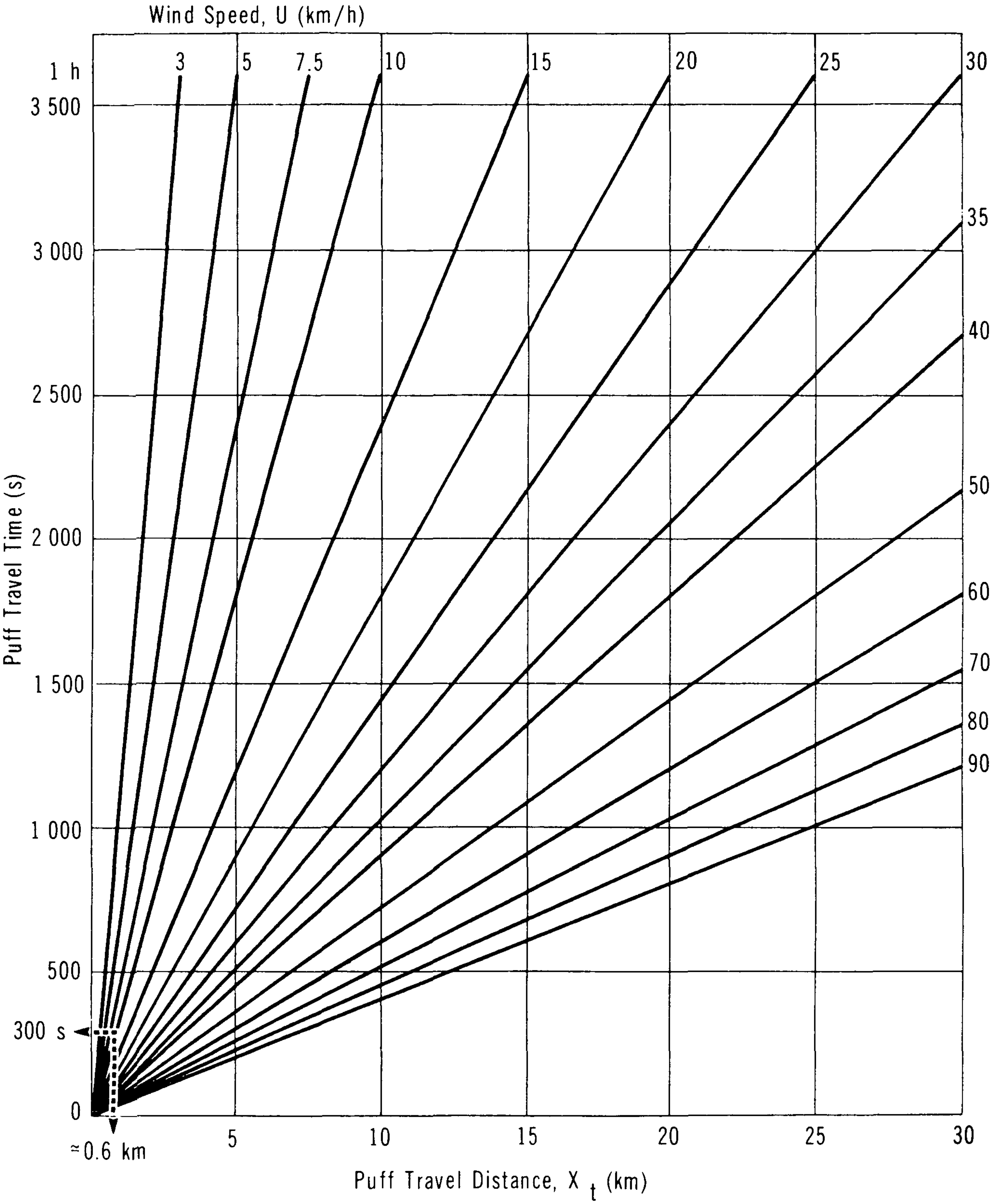
Step 4: Determine the wind speed (U) and direction (D)

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

Step 5: Determine the weather condition

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

PUFF TRAVEL TIME VS TRAVEL DISTANCE



Step 6: Determine the hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL
  C = 0.001 g/m^3 (TLV® = 0.0001 g/m^3; no LFL)

Step 7: Compute CU/Q

- $CU/Q = \frac{0.001 \times 2.1}{200} = 1.05 \times 10^{-5}\ m^{-2}$

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

- From Figure 13, with CU/Q = $1.1 \times 10^{-5}\ m^{-2}$ and weather condition F, $X_p \approx 22$ km

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

- With $X_p = 22$ km and r = 0.045 km, then
  $X_a = X_p - 10r = 22$ km - 10 (0.045 km) = 21.5 km

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

- Use Table 8
- with Q = 200 g/s and U = 2.1 m/s
  then $Q/U = \frac{200}{2.1} = 95$ g/m
- Then for weather condition F, the closest Q/U value is 100 g/m, which gives $(W/2)_{max} \approx 375$ m

Step 11: Determine the time since the spill

- t = 5 min x 60 s/min = 300 s

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

- Using Figure 14, with t = 300 s and U = 7.5 km/h, then $X_t = 0.6$ km (more accurately from Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 13: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (375 m) by the maximum hazard distance downwind of the area source (21.5 km) along the direction of the wind, as shown in Figure 15
- 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 16
- Note that the plume has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 165 minutes before the plume reaches the maximum downwind hazard distance of 21.5 km

FIGURE 15

TETRAETHYL LEAD

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

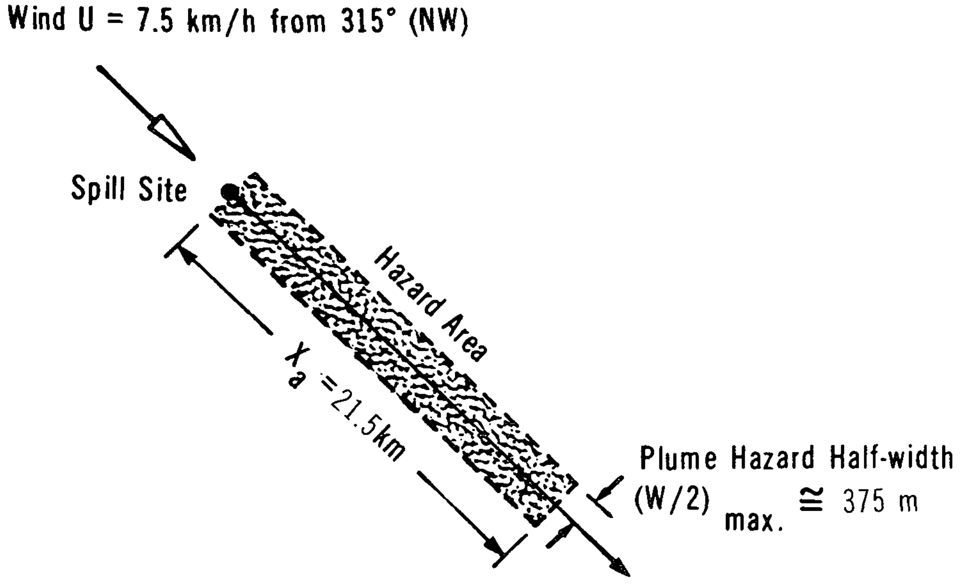
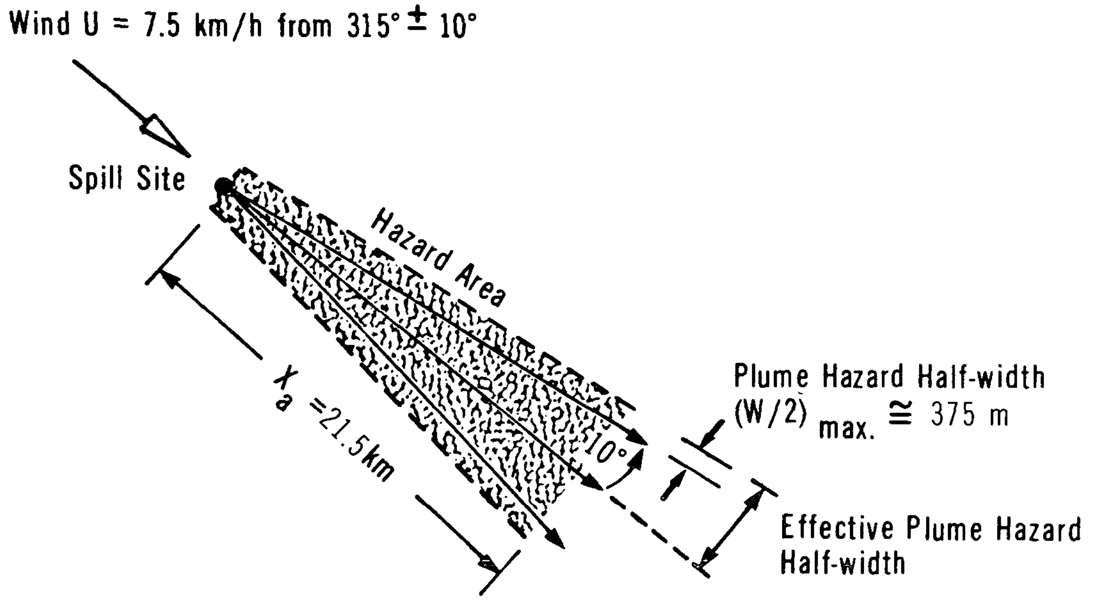


FIGURE 16

TETRAETHYL LEAD

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM



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

$= \underline{21.5 \times} \; 1000 \times \tan 10° + \underline{375}$

$= \underline{4170}$ m or 4.2 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, tetraethyl lead sinks and spreads across the stream bottom. Nomograms have been prepared to estimate the length and width of the zone of contamination in a non-tidal river. It represents the worst case scenario for the extent of the zone of contamination.

To estimate the zone of contamination on a river bed resulting from a spill of an insoluble, high density, liquid on water, the terminal fall velocities (V_t) of the discrete particles have been estimated using a mathematical model (Thibodeaux 1979). The fall velocity of an individual particle is a function of its specific gravity, size, and cross-sectional area, together with the density and viscosity of water. The drag force, tending to resist fall of the particle through water, varies for different flow regimes.

For any given tank puncture, the particle sizes are affected by the hole size, various physical properties of the chemical and of water, and the relative velocity with which the chemical impacts the water. Nomograms for fall velocity and spill width have been prepared for the smallest droplet size for any particular puncture size and thus maximize the estimated spill length and width. Details of the model are outlined in the Introduction Manual.

5.4.2 Nomograms.

5.4.2.1 Zone of stream bed contamination. The following nomograms are presented to calculate the length and width of the zone of contamination on the bed of a non-tidal river and in still water:

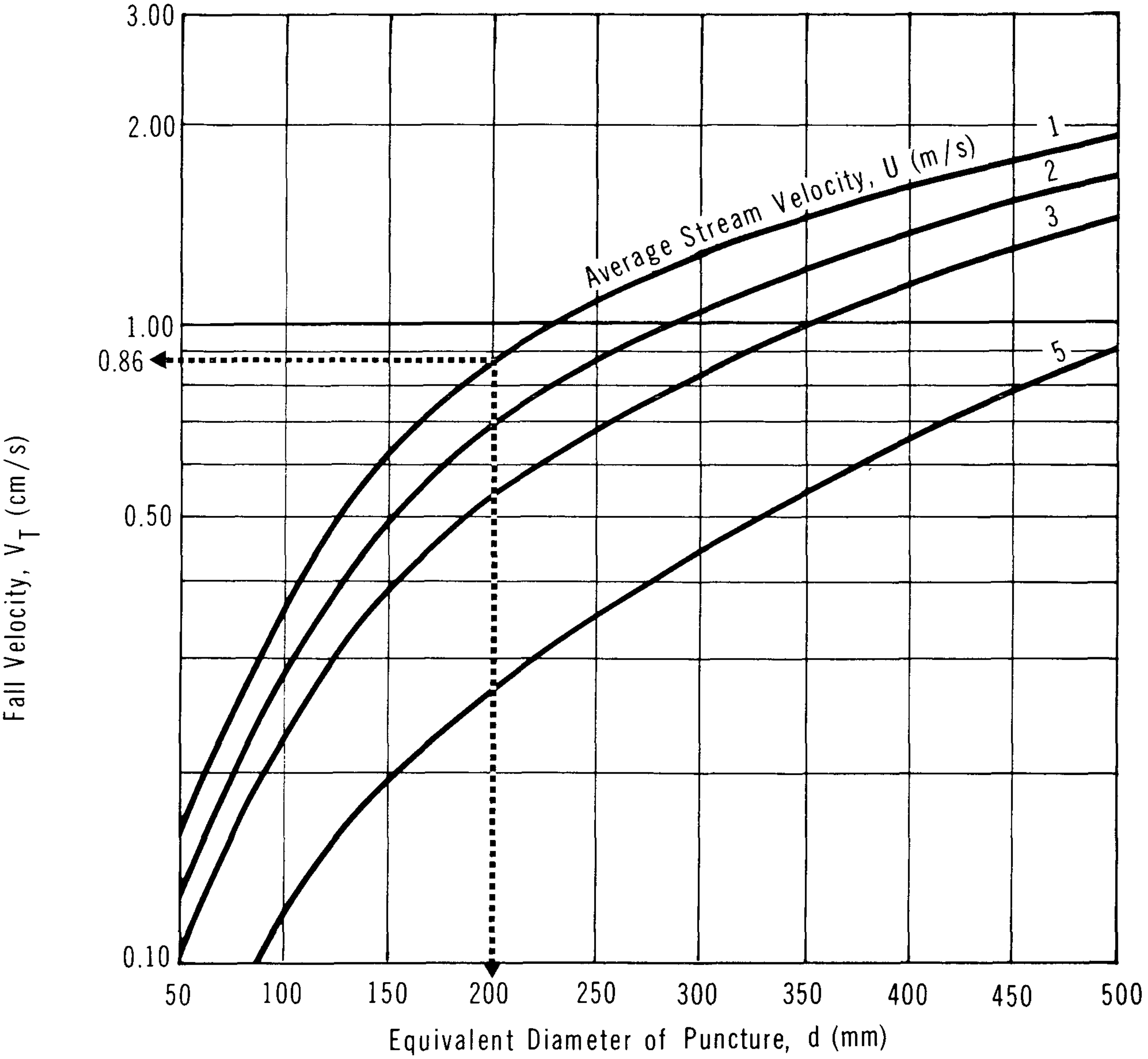
Figure 17:	fall velocity versus equivalent diameter of puncture for a range of average stream velocities
Figure 18:	settling time versus terminal fall velocity for a range of stream velocities
Figure 19:	downstream distance versus settling time for a range of average stream velocities
Figure 20:	spill width versus equivalent diameter of puncture for a range of stream depths

Figure 17: Fall velocity versus puncture size. The size of the smallest droplets is a function of the hole size, the physical characteristics of the chemical and of water, and the relative velocity with which the chemical impacts the water. For development of the nomogram, the exit velocity from the tank car was taken as the vertical component of velocity when the fluid jet hits the water surface. Figure 17 provides an estimate of the

FIGURE 17

TETRAETHYL LEAD

FALL VELOCITY vs PUNCTURE SIZE



terminal fall velocity in water of the smallest droplets of tetraethyl lead as a function of the diameter of the puncture and the average stream velocity. For stream velocities less than 1 m/s, the curve for 1 m/s may be used as a reasonable approximation.

Figure 18: Settling time versus terminal fall velocity. Based on a fall velocity (V_t) determined from Figure 17, the time (t) for the smallest droplets to settle to the bottom of a river of depth (d), neglecting turbulent mixing effects, can be estimated from Figure 18.

Figure 19: Distance versus settling time. Based on the settling time derived from Figure 18, the downstream distance (X) at which the smallest droplets of tetraethyl lead will reach the river bed can be determined from Figure 19 for a range of average stream velocities.

Figure 20: Spill width versus puncture size. For a given size of puncture, the width (W) of the zone of contamination on the stream bed can be established from Figure 19 for a range of stream depths. Again, the nomograph indicates a maximum spill width based on the spread of the smallest droplet sizes. The spill width (W) also provides an estimate of the diameter of the zone of contamination for spills on a still water body.

5.4.3 Sample Calculation.

A 20 tonne spill of tetraethyl lead has occurred in a river. The stream width is 250 m and the stream depth is 10 m. The average stream velocity is 0.5 m/s. Assuming the equivalent diameter of the puncture is 200 mm, how far downstream will the smallest droplets be carried before reaching the stream bed and what is the maximum width of the contaminated zone?

Solution

Step 1: Calculate the terminal fall velocity (V_t)

- Use Figure 17
- With diameter = 200 mm and $U \leq 1$ m/s, $V_t = 0.86$ cm/s

Step 2: Calculate the settling time

- Use Figure 18
- With $V_t = 0.86$ cm/s and depth = 10 m, t = 18 min

Step 3: Calculate the distance downstream for smallest droplets

- Use Figure 19
- With t = 18 min and V = 0.5 m/s, X = 570 m

FIGURE 18

TETRAETHYL LEAD

SETTLING TIME VS FALL VELOCITY

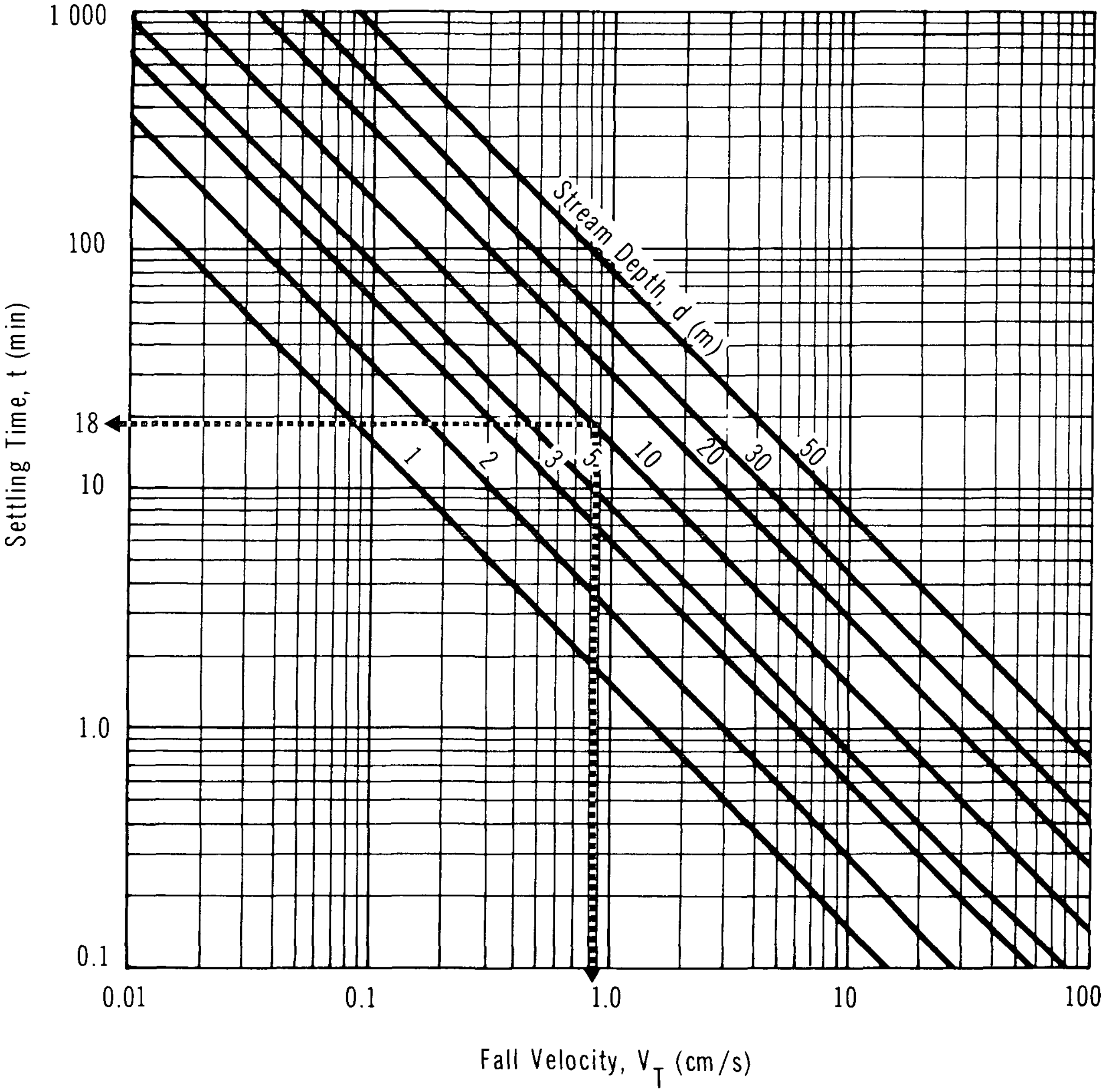


FIGURE 19

TETRAETHYL LEAD

DISTANCE VS SETTLING TIME

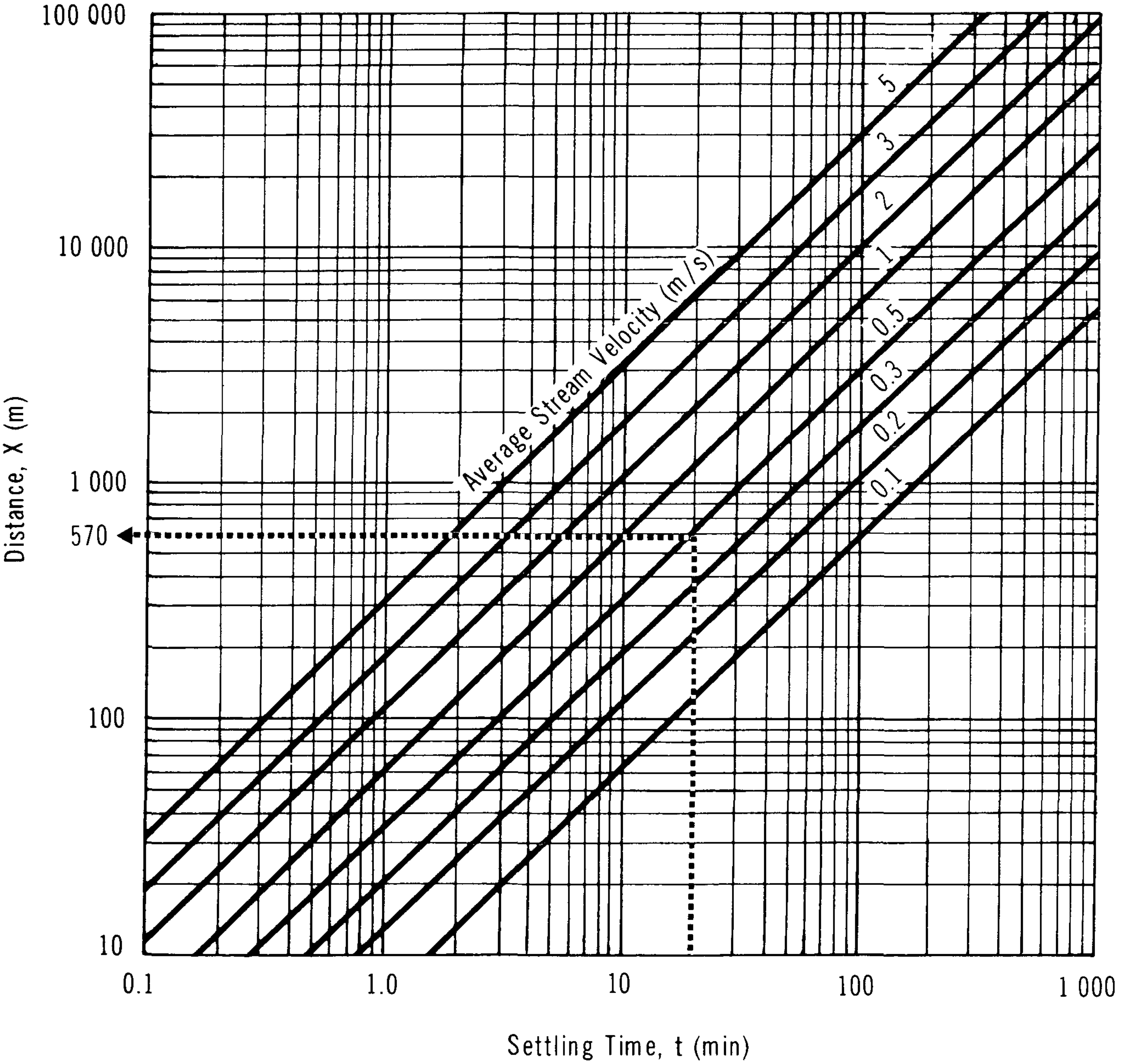
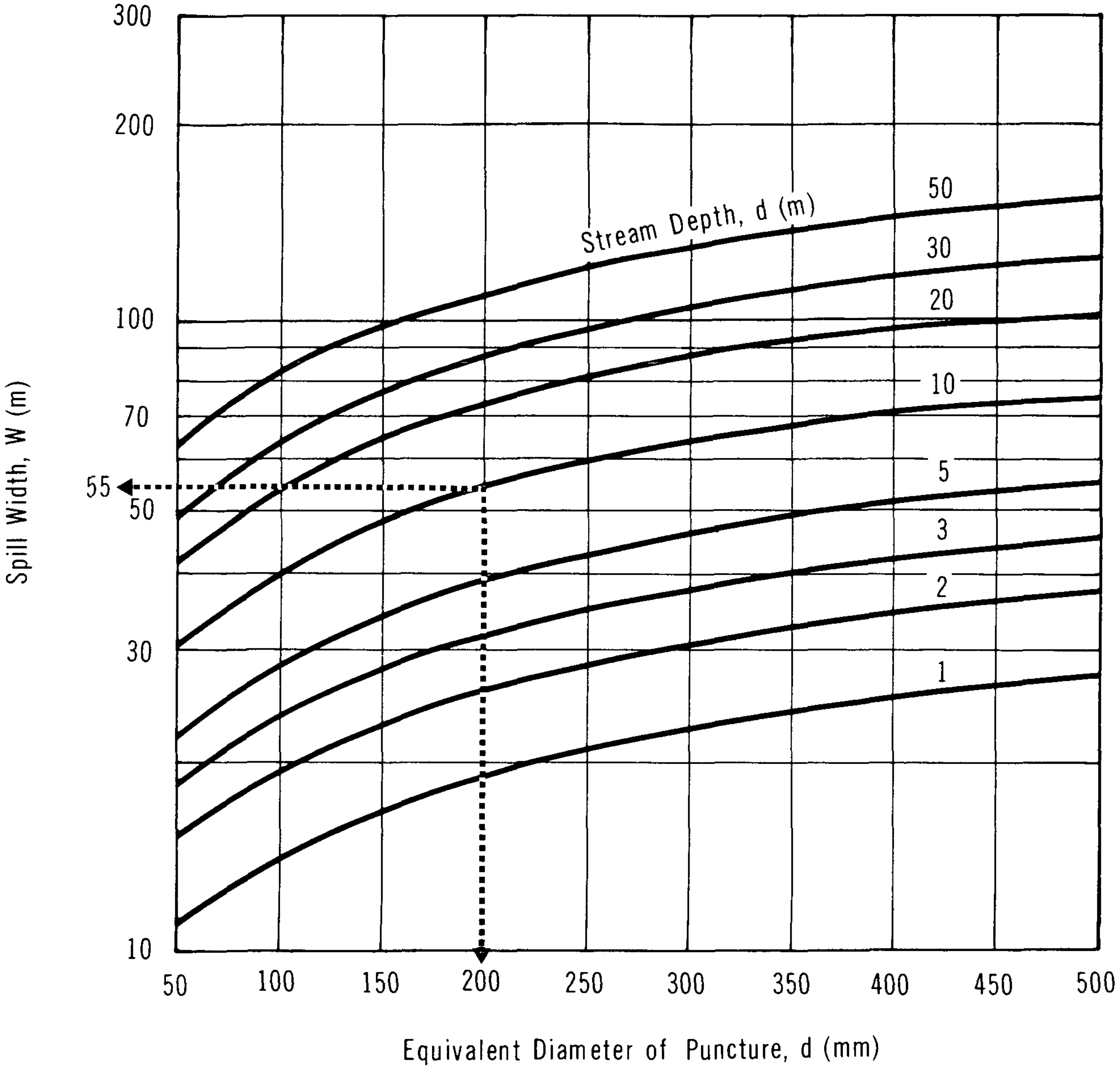


FIGURE 20

TETRAETHYL LEAD

SPILL WIDTH vs PUNCTURE SIZE



Step 4: Calculate the maximum spill width

- Use Figure 20
- With diameter = 200 mm and depth = 10 m, W = 55 m

5.5 Subsurface Behaviour: Penetration into Soil

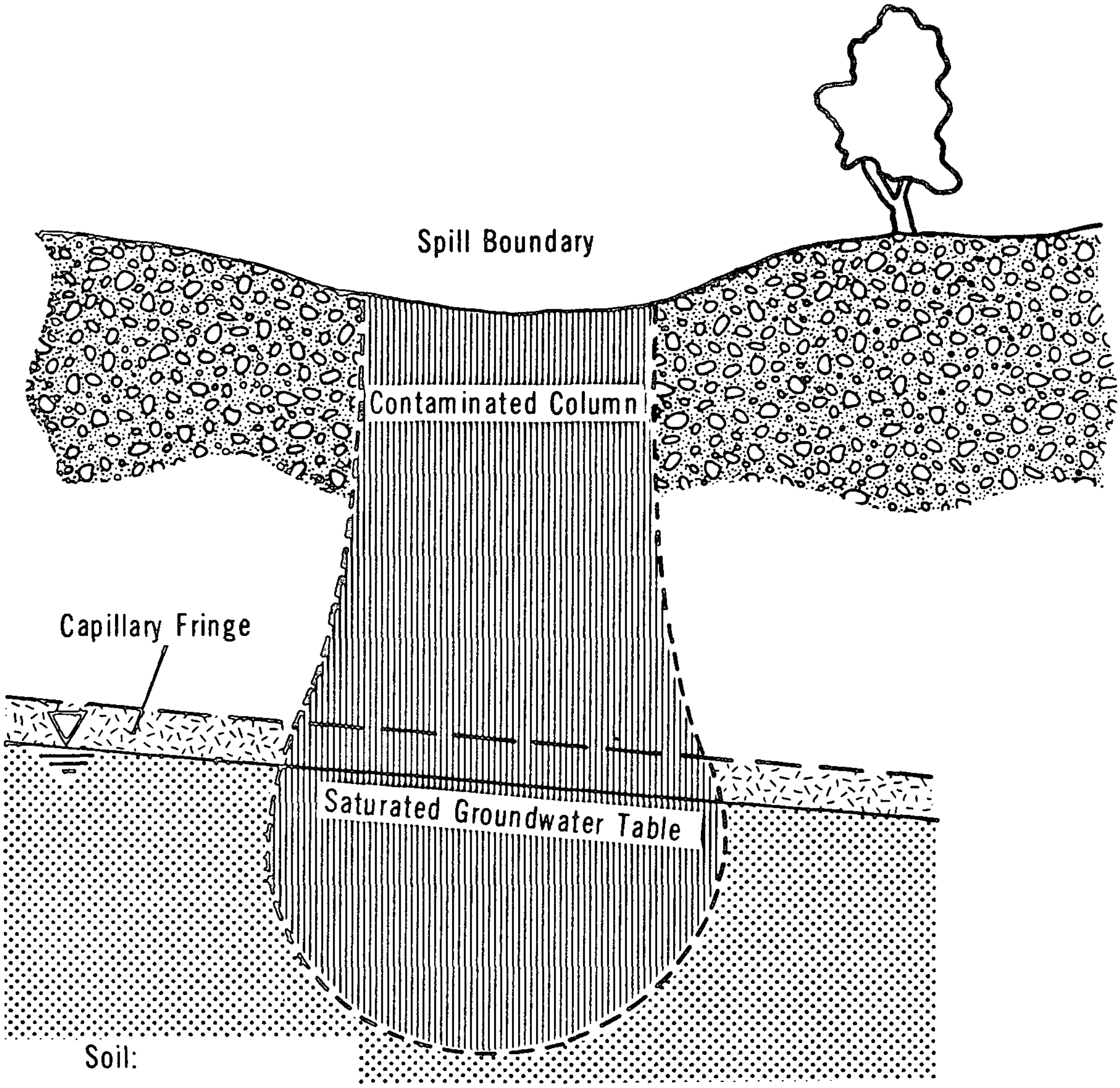
5.5.1 Introduction. Tetraethyl lead has a low solubility in water. Consequently, when spilled onto soil, its infiltration and transport downward through the soil involve multi-phase phenomena. The phases of concern are liquid, water, soil and gas or vapours.

Unfortunately, sufficient data do not exist to permit a detailed assessment of contaminant transport in a specific circumstance. A few extensive field investigations have been carried out, especially involving spills of oil, gasoline and PCBs. However, very limited information exists for tetraethyl lead. Consequently, it is necessary to simplify the soil and groundwater conditions and to express contaminant behaviour through analogy to other more extensively studied materials.

A pattern for the downward movement of immiscible fluids such as tetraethyl lead in soil has been prepared by comparison to oil spilled onto soil surfaces (Blokker 1971; Freeze and Cherry 1979). It is assumed that when the spill occurs, the soil contains water only up to its field capacity and that this condition prevails down to the groundwater table. The spilled tetraethyl lead fills the pores at the soil surface and begins to penetrate downward. It is assumed that the liquid moves downward through the soil as a saturated slug, but leaving behind a constant residual amount (S_o) within the soil pores. Downward transport will continue until the volume of tetraethyl lead spilled per unit area (B_o) equals the amount retained in the soil as S_o. Some lateral spreading may occur due to capillary action. If B_o is greater than the volume that can be retained as S_o above the groundwater table, the excess liquid will reach the saturated groundwater. Because it is denser than water, the tetraethyl lead will continue to move down slowly in the saturated zone. This is shown schematically in Figure 21.

5.5.2 Equations Describing Tetraethyl Lead 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.

SCHEMATIC SOIL TRANSPORT



Soil:

- –Coarse Sand
- –Porosity (n) = 0.35
- –Intrinsic Permeability (k) = 10^{-9} m^2
- –Field Capacity (θ_{fc}) = 0.075

*Column Contains Residual Tetraethyl Lead, S_o = 0.05

5.5.3 Saturated Hydraulic Conductivity of Tetraethyl Lead 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^2

The appropriate properties of tetraethyl lead are given in the chart below:

	Tetraethyl Lead	
Property	20°C	4°C
Mass density (ρ), kg/m^3	1660	1665
Absolute viscosity (μ), Pa•s	0.85×10^{-3}	1.1×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(1.9 \times 10^7)k$	$(1.5 \times 10^7)k$

5.5.4 Soils. Three soils were selected for this work. Their relevant properties are:

	Soil Type		
Property	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
Residual fraction (S_o), m^3/m^3	0.05	0.1	0.2

5.5.5 Penetration Nomograms. Nomograms for the penetration of tetraethyl lead into the unsaturated zone above the groundwater table were prepared for each soil. The nomograms show the total depth of penetration (B) versus penetration time (t_p) for various volumes spilled per unit area of soil (B_o). Temperatures of 4°C and 20°C were used.

$$v = -K_o \frac{(dh)}{(dl)} \qquad t_p = \frac{B}{v}$$

$$\frac{dh}{dl} = -1 \qquad B = \frac{B_o}{nS_o}$$

A flowchart for use of the nomograms is shown in Figure 22. The nomograms are presented in Figures 23, 24 and 25.

5.5.6 Sample Calculation. A 20 tonne spill of tetraethyl lead has occurred on coarse sandy soil. The temperature is 20°C; the spill radius is approximately 8.6 m. Calculate the depth and time of penetration.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- $T = 20°C$
- Mass density $\rho = 1660\ kg/m^3$
- $r = 8.6\ m$

Step 2: Calculate the volume and area of spill

- $V = \frac{mass}{\rho} = \frac{2 \times 10^4\ kg}{1660\ kg/m^3} = 12\ m^3$
- $A = \pi r^2 = 232\ m^2$

Step 3: Calculate the volumetric loading B_o

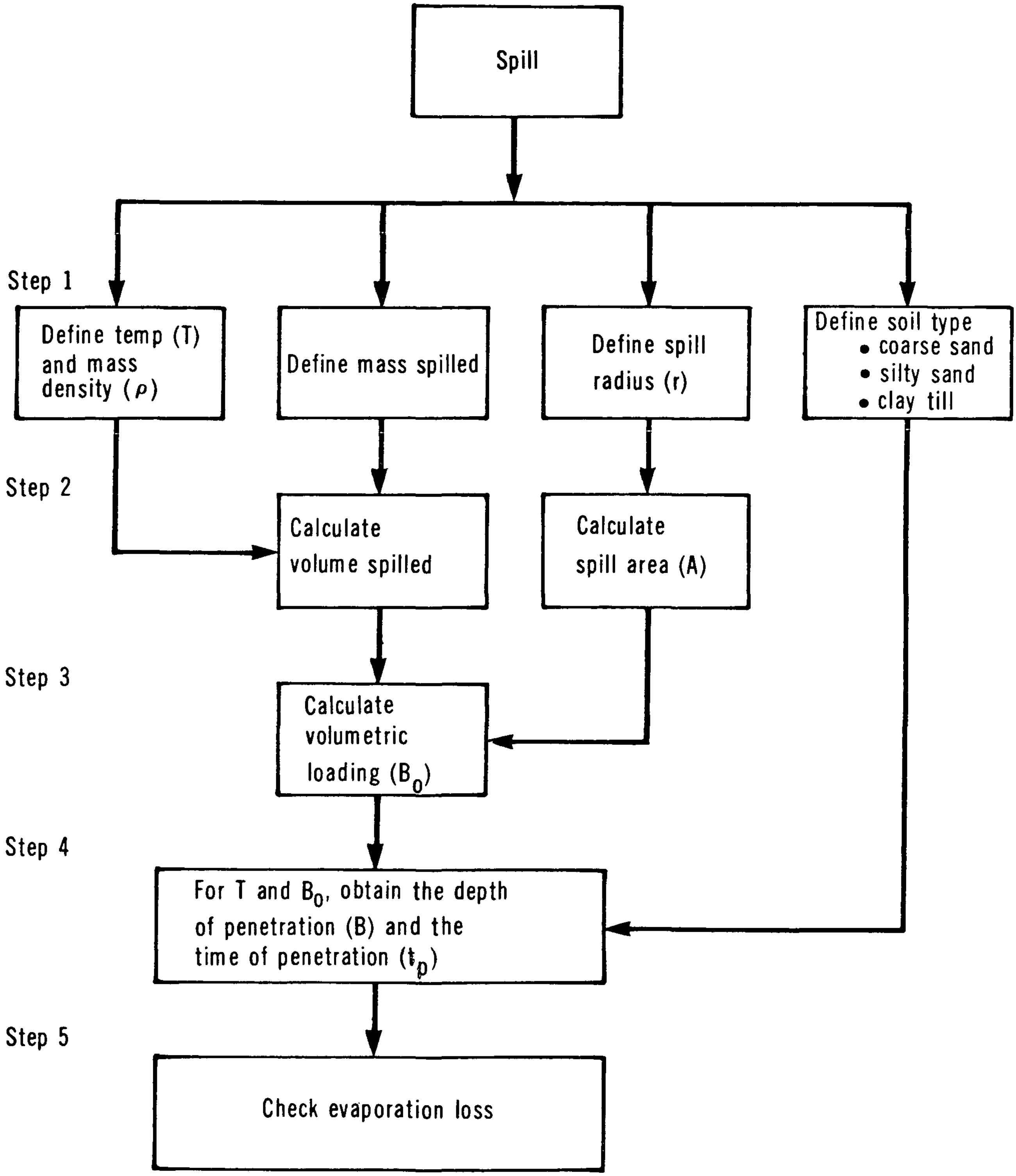
- $B_o = \frac{V}{A} = \frac{12}{232} = 0.05\ m^3/m^2$

Step 4: Estimate the depth of penetration (B) and time of penetration (t_p)

- For coarse sand, $B_o = 0.05\ m^3/m^2$
- $B = 2.8\ m$, $t_p = 2.5\ min$

FIGURE 22

FLOWCHART FOR NOMOGRAM USE



PENETRATION IN COARSE SAND

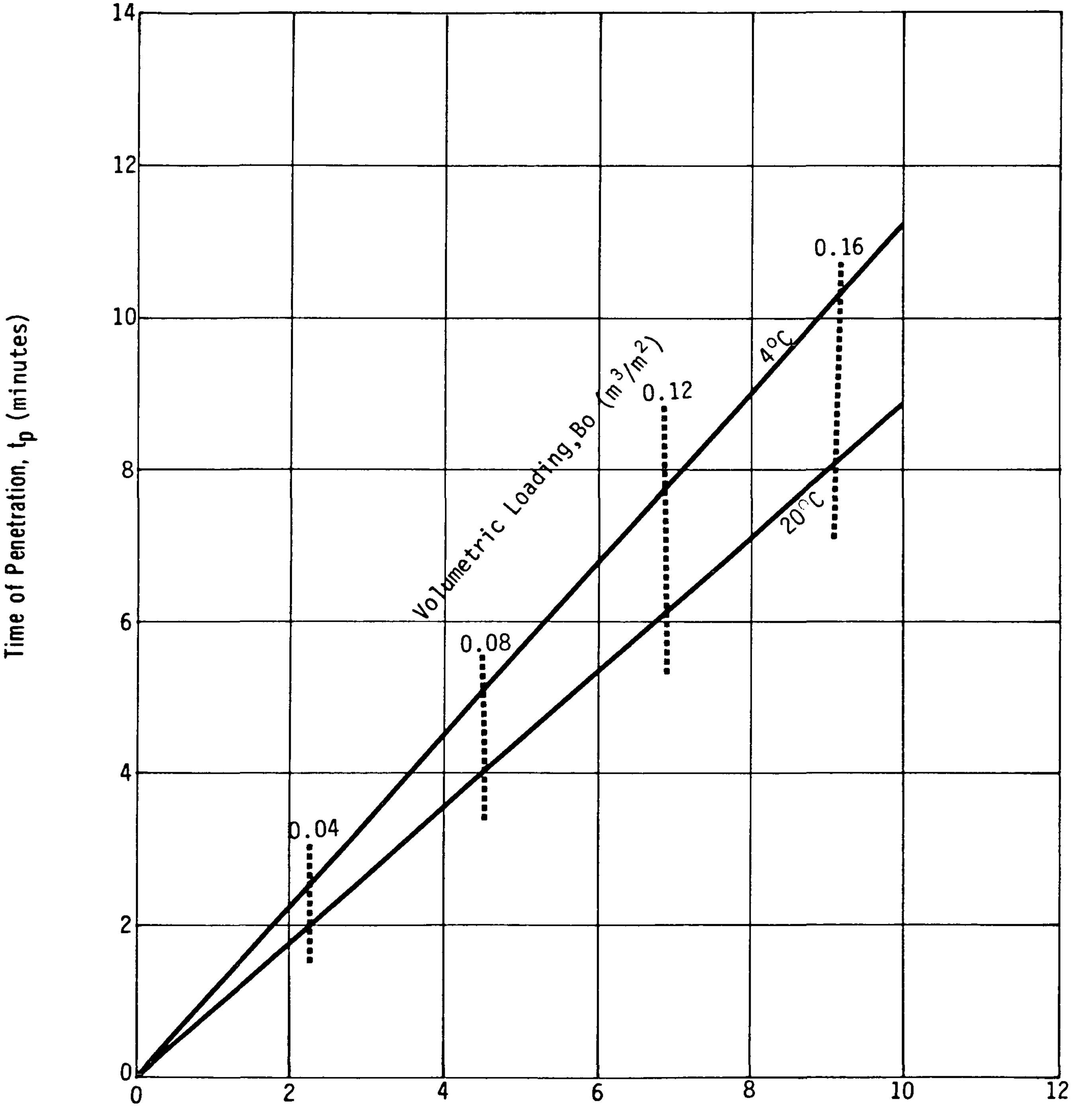


FIGURE 24

TETRAETHYL LEAD

PENETRATION IN SILTY SAND

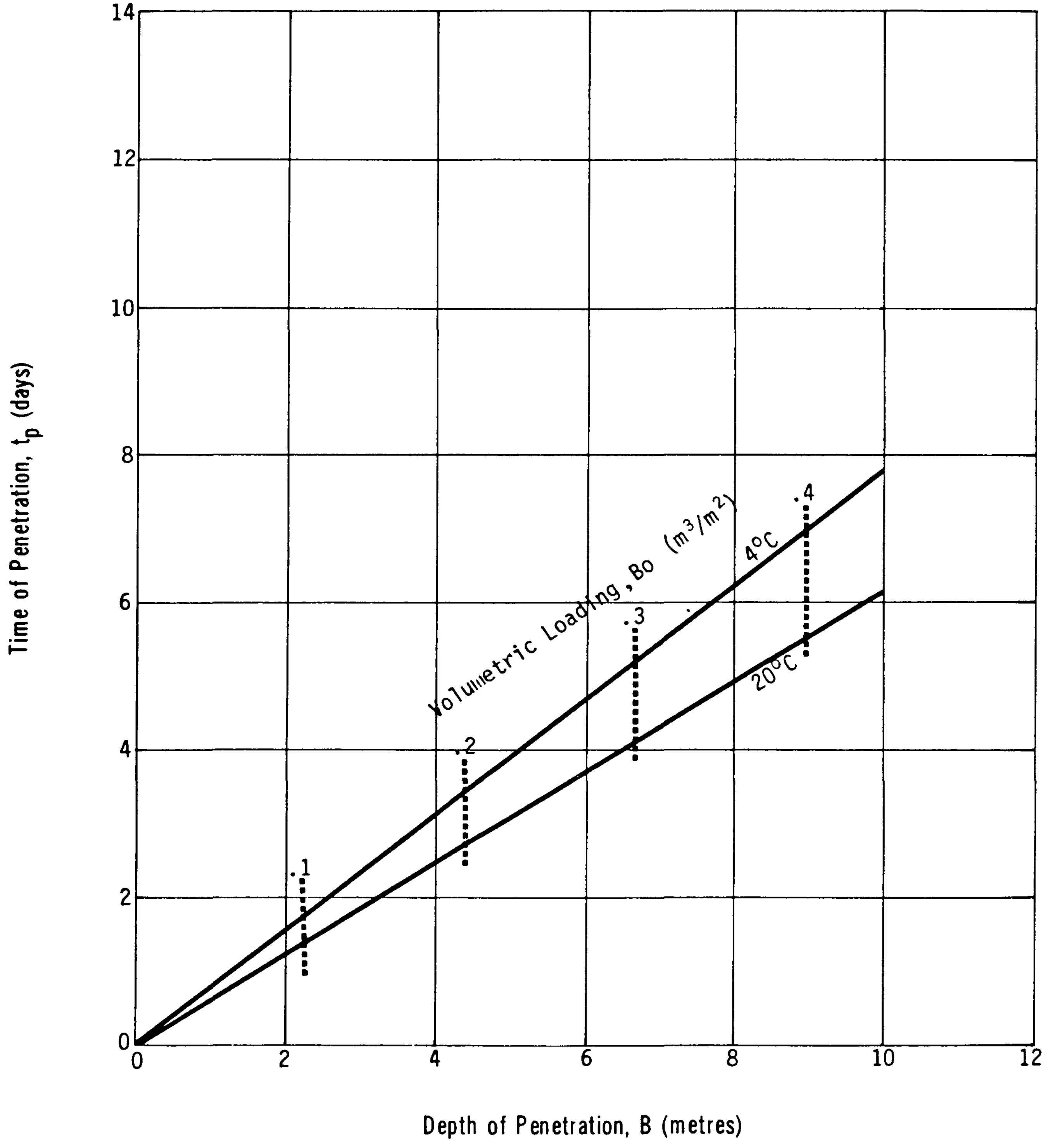
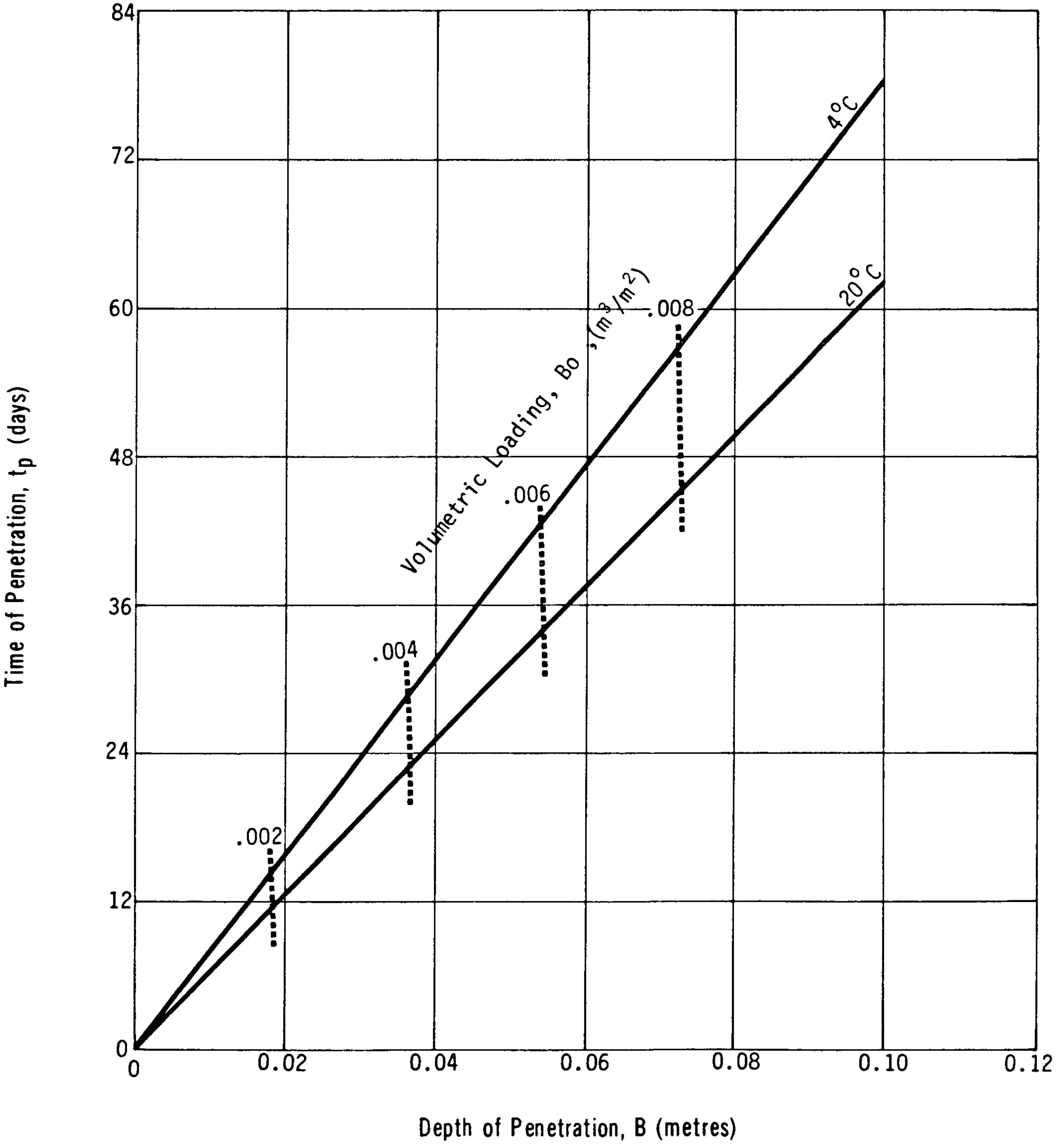


FIGURE 25

TETRAETHYL LEAD

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water.

6.1.1.1 North America. The permissible limit in surface water for public water supplies in Canada and the U.S. is 0.05 mg/L (WQCDB-2 1971; Drill 1979). The objective level for lead in Canadian drinking water is 0.001 mg/L (WQS 1979).

In both Canada and the U.S., the maximum level in drinking water for wildlife watering is 0.05 mg/L; the objective for livestock watering is the same value (WQS 1979). The lead limit for irrigation water is 5.0 mg/L for continuous use and 10 mg/L for intermittent use. The objective for recreational waters is 0.05 mg/L (GSWQ 1980).

6.1.1.2 Europe and USSR. The lead limit for drinking water and process water for food-processing plants in West Germany is 0.04 mg/L (MHSSW 1976).

In the USSR, the maximum permissible concentration of lead in reservoir waters is 0.1 mg/L (WQCDB-2 1971). The World Health Organization (WHO) European standard for lead in drinking water is 0.1 mg/L (WQCDB-2 1971).

6.1.2 Air Standards. Ontario limits total lead emissions to 10 $\mu g/m^3$ air (Ontario E.P. Act 1971). Emission standards in the U.S. have been proposed at 1 to 2 $\mu g/m^3$ (NAQS 1977).

6.2 Aquatic Toxicity

6.2.1 Guidelines and Objectives. The guideline limit in Canada is 0.03 mg/L for the protection of freshwater aquatic life, 0.05 mg/L for marine aquatic life, and 0.01 mg/L for "minimal risk of adverse effects" (WQS 1979). The objective for aquatic life is 0.005 mg/L in waters of hardness of less than 95 m/L ($CaCO_3$) and 0.01 for waters above this hardness rating (GSWQ 1980). In the U.S., the criterion for the protection of aquatic life is 0.75 $\mu g/L$ at a hardness of 50, and 3.8 $\mu g/L$ at a hardness of 100 (AWQCL 1980).

6.2.2 Toxicity Rating. Tetraethyl lead has been assigned a TL_m96 of less than 1 ppm (RTECS 1979).

6.2.3 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Freshwater Fish					
2.0	24	Bluegill	TL_m	tapwater	Jones 1971
1.4	48	Bluegill	TL_m	tapwater	Jones 1971
0.2	96	Bluegill	TL_m	tapwater	Jones 1971
Marine Species					
0.02 as (Pb)	96	Brown shrimp *(Crangon crangon)*	LC_{50}	Flow-through, 15°C, salinity 34.9 °/₀₀	Maddock 1980
0.10 as (Pb)	96	Mussel *(Mytilus edulis)*	LC_{50}	Flow-through, 15°C, salinity 34.9 °/₀₀	Maddock 1980
0.23 as (Pb)	96	Plaice *(Pleuronectes platessa)*	LC_{50}	Flow-through, 15°C, salinity 34.9 °/₀₀	Maddock 1980
0.025	tns	Brine shrimp *(Artemia salina)*	no effect	-	JWPCF 1979
0.085	tns	Brine shrimp *(Artemia salina)*	LC_{50}	-	JWPCF 1979
0.010	tns	Fish larvae *(Morone labrax)*	No effect	-	JWPCF 1979
0.065	tns	Fish larvae *(Morone labrax)*	LC_{50}	-	JWPCF 1979
Microorganisms					
1.3	6	Algae *(Phaeodactylum tricornutum)*	EC_{50}, reduction in photosynthesis	Flow-through, 15°C, salinity 34.9 °/₀₀	Maddock 1980

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.03	tns	Mixed marine bacteria	no effect on respiration rate	saltwater	JWPCF 1981
0.08	tns	Mixed marine bacteria	50% change in respiration	saltwater	JWPCF 1981
0.1	tns	Algae *(Dunaliella tertiolecta)*	no effect on photosynthesis	saltwater	JWPCF 1981
0.15	tns	Algae *(Dunaliella tertiolecta)*	50% reduction in photosynthesis	saltwater	JWPCF 1981
<0.3	4	Algae *(Ankistrodesmus polcatus)*	EC_{50}	freshwater	Verschueren 1984
0.1 (as Pb)	96	Algae (not specified)	LC_{50}	freshwater	Verschueren 1984

6.2.4 Aquatic Studies. Tetraethyl lead is more toxic to aquatic species than are most other forms of lead, primarily because it is lipid-soluble. The acute toxicity of lead, by itself, is lower as the hardness increases. The toxicity of the lead ion ranges from 0.2 to 236 mg/L for freshwater species and from 0.5 to 27 mg/L for saltwater species. This is 10 to 100 times less toxic than tetraethyl lead (AWQCL 1983).

The biocencentration factor (BCF) for three marine species has been measured (Maddock 1980):

BCF	Species
650	Shrimp *(Crangon crangon)*
120	Mussel *(Mytilus edulis)*
130	Plaice *(Pleuronectes platessa)*

The bioconcentration factor for lead alone has been measured to be 18 to 257 (AWQCL 1983). On the basis of this, tetraethyl lead appears to have a much greater bioconcentration potential than lead alone. Lead itself has been extensively studied in the aquatic milieu, whereas tetraethyl lead has not (AQC 1977; NSF 1977; Rolfe 1977).

6.3 Mammalian Toxicity

All the following data are for lead only; tetraethyl lead may be much more toxic on an acute basis. The suggested maximum level of tetraethyl lead in drinking water for livestock is 2 ppm (OHM-TADS 1981).

Dosage (lead)	Animal	Effect	Reference
0.18 mg/L	Cattle	chronic lead poisoning in soft water	Pierse
200 to 400 mg/kg	Calves	lethal dose	Botts 1977
60 to 800 mg/kg	Cattle	lethal dose	Botts 1977
516 ppm in food	Horse	lethal dose	Botts 1977
2.4 mg/kg/d (6 mo)	Horse	lethal dose	Botts 1977
5000 ppm in food	Chickens	produced renal necrosis	Botts 1977
8 mg/kg b.w./d (50 d)	Sheep	produced renal necrosis	Botts 1977
600 mg/kg/d	Dog	produced renal necrosis	Botts 1977
8 to 12 mg/kg/d (25 to 28 d)	Ducks	produced renal necrosis	Botts 1977

6.4 Plant Toxicity

One study using algae indicated that tetraethyl lead was toxic under sunlight but not while in darkness. The conclusion was that the photodegradation products (primarily triethyl lead) were more toxic than tetraethyl lead itself (JWPCF 1981). Plants (*Bougainvillea* sp.) exposed to 7 ppm TEL vapour at 25°C for 3 days exhibited 14 percent defoliation or abscission. Fourteen days were required for a full recovery (Ewing 1974). In another study, onion bulbs exposed to about 1 to 10 ppm (10^{-6} to 10^{-7} M) tetraethyl lead showed disturbances (Ewing 1974).

Lead, by itself, has been shown to be absorbed by plants through the root system and not so definitively through the leaves. Under certain soil conditions (e.g., low pH, low cation exchange capacity, low organic content and low phosphate levels), lead absorption through the roots is very high. Lead is known to be deposited (and thus made relatively innocuous) at the roots by the formation of lead/phosphorus compounds (NSF 1977).

6.5 Degradation

Tetraethyl lead, especially in the vapour phase, degrades in sunlight to the even more toxic triethyl lead and ultimately to inorganic lead compounds (OHM-TADS 1981). Breakdown in water gives a half-life on the order of days (Grove 1980). Decomposition in water is thought to follow the scheme (Verschueren 1984):

$$(C_2H_5)_4\,Pb \rightarrow (C_2H_5)_3Pb^+ \rightarrow (C_2H_5)_2Pb^{2+} \rightarrow Pb^{2+}$$

In an experiment, a 1 mg/L solution showed the following levels after 2 days: TEL, 0.626 mg/L; $(C_2H_5)_3Pb+$, 0.39 mg/L; $(C_2H_5)_2Pb^{2+}$, <0.005 mg/L; and Pb^{2+}, 0.057 mg/L (Verschueren 1984).

6.6 Long-term Fate and Effects

Tetraethyl lead will ultimately degrade to lead. Lead will bioaccumulate and will be passed on in the food chain (OHM-TADS 1981).

7 HUMAN HEALTH

Tetraethyl lead has only a slight odour (Doc. TLV 1981); it is not sufficiently distinctive at concentrations below exposure guidelines to be considered as having a good warning property. Unlike inorganic lead forms, TEL is a lipid solvent and can enter the body not only when inhaled but also when absorbed through intact skin. It is generally a powerful poison and a solvent for fatty materials. Absorption through any route of exposure, due to repeated low doses or a single high dose, can cause a series of central nervous system disorders (USDHEW 1977).

TEL was selected for carcinogenesis bioassay at the request of OSHA and the U.S. National Cancer Institute in September 1978 (RTECS 1979), but testing was dropped (USDHEW 1980). One test involving mice has been reported as positive for carcinogenesis (RTECS 1979). No mutagenicity or teratogenicity testing was documented in the literature, although NIOSH/OSHA (1981) does report that "fetal damage may occur when a mother is exposed to tetraethyl lead, by analogy to methyl mercury". No recent monographs or reviews of TEL toxicity were found.

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. Only acute (short-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where appropriate, with the exception of carcinogenicity and teratogenicity data. Data on lead exposure are generally not included. A number of reviews on lead have been published (WHO 1977; Blackwood 1979; Harrison 1981).

7.1 Recommended Exposure Limits

The exposure standards for tetraethyl lead are based upon its effect on the central nervous system. 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, skin)	USA-ACGIH	0.100 mg/m^3 (as Pb)	TLV 1981
PEL (8 h)	USA-OSHA	0.075 mg/m^3	NIOSH/OSHA 1981

Guideline (Time)	Origin	Recommended Level	Reference
Permissible 8 h limit (skin) concentrations	B.C.	0.1 mg/m^3 (as Pb)	B.C. 1980
Average concentration	Quebec	0.1 mg/m^3 (as·Pb)	Quebec 1979
15 minute average contamination limit	Saskatchewan	0.1 mg/m^3 (as Pb)	Sask. 1981
TWA	Ontario	0.10 mg Pb/m^3	Ont. Reg. 1981
Short-term Exposure Limits (STEL)			
STEL (15 min, skin)	USA-ACGIH	0.3 mg/m^3 (as Pb)	TLV 1981
Maximum Concentration of exposure (15 min, not more than 4/d, and shall not occur until 60 min have elapsed from time of last previous exposure to such concentration	Ontario	0.30 mg Pb/m^3	Ont. Reg. 1981
Maximum concentration	Quebec	0.3 mg/m^3 (as Pb)	Quebec
Permissible concentration, (15 min limit, skin)	B.C.	0.3 mg/m^3 (as Pb)	B.C. 1980
Other Human Toxicities			
IDLH	USA-NIOSH	40 mg/m^3	NIOSH Guide 1978
LD_{LO}		1470 µg/kg	RTECS 1979

7.2 Irritation Data

7.2.1 Skin Contact. (Absorption of TEL through the intact skin can also result in systemic poisoning. Data relating to this type of exposure have been reported in Section 7.4.4).

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Itching, inflammation and blisters.	Lefèvre 1980
Unspecified	Liquid alkyl lead may penetrate the skin without producing applicable local injury.	USDHEW 1977
Unspecified	Causes smarting of the skin and first-degree burns on short exposure; may cause secondary burns on long exposure.	CHRIS 1978

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	May irritate eyes.	NIOSH/OSHA 1981
Unspecified	Irritation of conjunctiva.	Lefèvre 1980
Unspecified	Vapour is irritating to eye. Liquid will burn eyes.	CHRIS 1978
SPECIES: Rabbit		
In "high-test gasoline" (up to 10 times in 5 min)	Immediate pain and blepharospasm lasting several minutes. With repeated exposure, conjunctival hyperemia and moderate flocculent discharge, but no damage to cornea or conjunctiva.	NIOSH/OSHA 1981

7.3 Threshold Perception Properties

7.3.1 Odour. Odour characteristics: Sweet, etheral odour when pure; may develop rotten-cabbage odour from the presence of mercaptans. Odour is weak and variable (Barry 1973).

7.3.2 Taste. No data.

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
100 mg/m^3 (as lead) (1 h)	May produce illness.	Doc. TLV 1981
100 mg/m^3 (1 h)	Acute intoxication. The onset of symptoms may be delayed for up to several days after exposure. The milder manifestations of intoxication are insomnia, lassitude, lurid dreams, dream-like waking states of anxiety, tremor, hyperreflexia, spasmodic muscular contractions, bradycardia, hypotension, hypothermia, pallor, nausea, and anorexia. More severe intoxication causes recurrent or nearly continuous episodes of disorientation, hallucinations, facial contortions, and intense hyperactivity which requires that the individual be restrained. Such episodes may convert abruptly into manic or violent convulsive seizures which may terminate in coma and death.	NIOSH/OSHA 1981
SPECIES: Rat		
850 mg/m^3 (60 min)	LC_{50}	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
650 mg/m^3 (7 h)	LC_{LO}	RTECS 1979
<u>Chronic Exposures</u>		
SPECIES: Human		
Unspecified (17.9 yr average)	In 592 workers, urinary lead levels did not exceed 180 μg/L. The incidence of death in this group and in a control group of employees was less than expected for the general population; there were no peculiarities in the specific causes of death in either group.	NIOSH/OSHA 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Increased urinary output of lead, nausea, vomiting and death.	AAR 1981
SPECIES: Rabbit		
30 mg/kg	LD_{LO}	RTECS 1979
SPECIES: Rat		
17 mg/kg	LD_{LO}	RTECS 1979
17 mg/kg	Approximate acute LD_{50}. All rats on TEL displayed increasing irritability, hyperactivity, tremors, spasticity, arched backs, and prostration. All symptoms had abated within 2 weeks.	Patty 1981

Exposure Level (and Duration)	Effects	Reference
12.3 mg/kg	LD_{50}	Doc. TLV 1981
11 mg/kg	LD_{LO} to 6/160 pregnant rats	Sax 1984
7.5 mg/kg	LD_{LO} to 12/140 pregnant rats	Sax 1984

7.4.3 Subcutaneous.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
32 mg/kg	LD_{LO}	RTECS 1979
SPECIES: Mouse		
100 mg/kg	TD_{LO}	Sax 1984
86 mg/kg	LD_{LO}	RTECS 1979

7.4.4 Skin. Absorption of TEL through intact skin has resulted in systemic poisoning. The ability of tetraethyl lead to penetrate the skin makes reliance on airborne concentration impractical in many situations (Doc. TLV 1981).

Exposure Level (and Duration)	Effects	Reference
SPECIES: Dog		
547 mg/kg	LD_{LO}	RTECS 1979
SPECIES: Rabbit		
830 mg/kg	LD_{LO}	RTECS 1979
0.7 g/kg	Lethal dose	Doc. TLV 1981
SPECIES: Guinea Pig		
995 mg/kg	LD_{LO}	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
1.03 mg/L (vapour)	Resulted in an absorption equivalent to a dose of 3.19 mg/kg (absorption ratio of 2 to 4).	Bell 1978

7.4.5 Mutagenicity, Teratogenicity, Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Fetal damage may occur when a mother is exposed to tetraethyl lead (by analogy to methyl mercury).	NIOSH/OSHA 1981
SPECIES: Mouse		
86 mg/kg (21 d intermittently)	Subcutaneous administration resulted in carcinogenic LD_{LO}.	RTECS 1979

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated. Symptoms may be delayed, depending on severity of exposure, from within 6 hours to 10 days (Barry 1973).

7.5.1 Inhalation.

1. Irritation of nose and throat.
2. Burning sensation.
3. Lassitude.
4. Insomnia, nightmares (Lefèvre 1980).
5. Pallor.

6. Nausea.
7. Dream-like waking states of anxiety (NIOSH/OSHA 1981).
8. Tremor.
9. Hyperreflexia (NIOSH/OSHA 1981).
10. Spasmodic muscular contractions (NIOSH/OSHA 1981).
11. Hypotension.
12. Hypothermia.
13. Anorexia.
14. Bradycardia.
15. Continuous episodes of disorientation (NIOSH/OSHA 1981).
16. Hallucinations.
17. Facial contortions (NIOSH/OSHA 1981).
18. Intense hyperactivity.
19. Manic or violent convulsive seizures.
20. Coma.
21. Death.

7.5.2 Ingestion.

1. Headache.
2. Metallic taste (Barry 1973).
3. Signs of pallor.
4. Restlessness.
5. Shivering.
6. Insomnia and disturbance in sleep patterns (Harrison 1981).
7. Delirium (Lefèvre 1980).
8. Nausea and vomiting (AAR 1981).
9. Tremors and muscular weakness (Harrison 1981).
10. Convulsions.
11. Death.

7.5.3 Skin Contact.

1. Itching.
2. Inflammation and blisters (Lefèvre 1980).
3. Insomnia (AAR 1981).
4. Excitability.

5. Delirium (AAR 1981).
6. Coma.
7. Death.

7.5.4 Eye Contact.

1. Irritation.
2. Watering of eyes.
3. Inflammation of conjunctiva (Lefèvre 1980).

7.6 Human Toxicity to Decay or Combustion Products

Sunlight decomposes tetraethyl lead to toxic triethyl lead (OHM-TADS 1981). Toxic airborne substances (such as lead fumes) may be released in a fire involving tetraethyl lead (NIOSH/OSHA 1981).

7.6.1 Lead and Triethyl Lead. Lead is suspected of being carcinogenic (Patty 1981). It produces a brittleness of red blood cells so that they hemolyze with slight trauma. In addition, lead has a damaging effect on the organs or tissues it contacts (Sax 1984). The TLV® for lead is 0.15 mg/m^3 (8 h - TWA) and 0.45 mg/m^3 (STEL) (TLV 1983).

The decomposition products of TEL (i.e., mono-, di-, and triethyl lead compounds) in dust form may be inhaled and result in irritation of the upper respiratory tract and possibly paroxysmal sneezing. This dust, when in contact with moist skin or ocular membranes, may cause itching and burning or transient redness (USDHEW 1977). No specific TLV®s are listed for these lead compounds (TLV 1983).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Tetraethyl Lead with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Fire		●												Sax 1984
Heat						●								Sax 1984
UV Light			●			●							Can explosively decompose if left long-term (several days).	Bretherick 1979
CHEMICAL GROUPS														
Halogens											●		In bulk and with purer forms of TEL.	Ethyl Corp.; Ethyl MSDS 1972
Oxidizing Agents											●			Sax 1984

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 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. Tetraethyl lead is a combustible liquid (NFPA 1978). Temperatures above 100°C cause decomposition of tetraethyl lead and development of pressure that may cause containers to burst. Contact with strong oxidizers, such as potassium permanganate, may cause fires and explosions. Toxic airborne substances, such as lead fumes, lead oxybromides, oxychlorides, etc., may be released in a fire involving tetraethyl lead (NIOSH/OSHA 1981).

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

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

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

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (Ethyl MSDS 1972). Use water spray to reduce vapours and to protect men effecting the shut-off (ERG 1980; NFPA 1978). Fluorocarbon water foam can also be applied to diminish vapours and fire hazard (EPA 670/2-75-042).

9.1.3.2 Spills on land. For small spills, absorb spilled material in vermiculite, sand or other noncombustible absorbent material and shovel into covered containers for disposal (ERG 1980).

For large spills, contain if possible by forming mechanical barriers to prevent spreading. Using extreme caution, remove the liquid with pumps and suction equipment. Contaminated soil should be removed as well (EPA 670/2-75-042).

9.1.3.3 Spills in water. Contain, if possible, by forming natural deep water pockets or using sand bag barriers to trap material at the bottom. Remove trapped material with suction hoses (EPA 670/2-75-042).

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills on land. On flat surfaces such as floors, the following treatment is recommended (Ethyl Corp.): For spills on dry surfaces, cover the contaminated area with naphtha (Stoddard solvent) containing iodine (0.2 percent) in solution. An excess of lead alkyl will decolorize the iodine solution; therefore, it is necessary to maintain an excess of iodine in naphtha over the area. After 30 minutes, collect the residues for disposal. Rinse the treated area with a solution of sodium thiosulphate (5 percent) and sodium bicarbonate to remove the excess iodine.

If the surface was wet prior to the spill and the temperature is above 16°C, cover the contaminated area with iodine in acetic acid solution (0.5 percent). Remove the excess iodine by using a solution of sodium thiosulphate (5 percent) and sodium bicarbonate (5 percent). If the temperature of the wet surface is below 16°C, cover the contaminated area with a solution of iodine in isopropyl alcohol. Remove the excess iodine in the same manner as above.

9.1.4.2 Spills in water. After containment of spilled material at the bottom, remove using suction equipment. If solubilized, apply activated carbon at 10 percent the spill amount over the region occupied by 10 mg/L or greater concentrations. Then use mechanical dredges or lifts to remove the carbon (EPA 670/2-75-042). Calcium-EDTA may be helpful in complexing the lead (OHM-TADS 1981).

9.1.4.3 General. For treatment of contaminated water, gravity separation of the solids followed by dual media filtration and carbon adsorption is recommended (EPA 600/2-77-227). The recommended carbon ratio is 1.0 kg to 3.5 kg soluble material. Further treatment with calcium hydroxide to precipitate lead and then hydrochloric acid to lower the pH to 7.0 is also recommended prior to discharge. Wastewater from backwash of the adsorption and filtration units is returned to the gravity separator.

9.1.5 Disposal. Tetraethyl lead must never be discharged directly into sewers or surface waters. It can be dissolved in a flammable solvent and sprayed into an incinerator equipped with an afterburner and alkali scrubber (OHM-TADS 1981). Solids such as contaminated clothing, sorbents, etc., should be incinerated in a similar way. Metal items should be decontaminated with solvent and the solvent disposed of as noted above.

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

If the spill material is known to be tetraethyl lead:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with undiluted liquid tetraethyl lead or its solutions (NIOSH/OSHA 1981).
- Splash-proof safety goggles are recommended where liquid tetraethyl lead may contact the eyes (NIOSH/OSHA 1981; GE 1979).
- Neoprene-coated, liquid-proof gloves are recommended when handling tetraethyl lead (Ethyl MSDS 1972).
- Nonimpervious clothing which becomes contaminated with undiluted liquid tetraethyl lead or its solutions should be removed immediately and not reworn (NIOSH/OSHA 1981). It is wisest to dispose of the clothing by incineration (CCPA 1983).

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

Condition	Minimum Respiratory Protection* Required Above 0.075 mg/m^3
Vapour Concentration	
0.75 mg/m^3 or less	Any supplied-air respirator.
	Any self-contained breathing apparatus.
3.75 mg/m^3 or less	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.

Condition	Minimum Respiratory Protection* Required Above 0.075 mg/m^3
40 mg/m^3 or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m^3** 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 full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapours. Any escape self-contained breathing apparatus

* Only NIOSH-approved 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 tetraethyl lead; 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 40 mg/m^3, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

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 **The CAVTAT Incident** (Harrison 1980; Cleaver 1980)

The freighter CAVTAT carrying 274 drums (45 gallons each) of tetraethyl lead, and a larger number of drums of tetramethyl lead collided with another vessel in the Mediterranean in 1974. The CAVTAT sank in 95 m of water, 3 hours after the incident. Of the total number of drums, 496 were stored on deck and 404 were in the holds. The drums were constructed of 2.5 mm steel plate and had been zinc-sprayed.

Not until 1 year later were divers able to go to the wreck and assess damage. Meanwhile, laboratory and field tests were conducted to assess the effect on the drums. It was concluded that the drums could withstand the pressure of 95 m of water and, except for pinhole leaks, could withstand corrosion for a long period of time - perhaps up to 10 years.

Samples of marine fauna and sediment were collected over a 2-year period; no correlation between lead content and proximity to the wreck could be established. Modelling studies showed that mass transfer of lead from a pool surface under water would be such that contamination would not result 500 m away.

Recovery began in 1977; in that year, 495 of the 496 drums stowed on deck were recovered. Two were empty as a result of mechanical damage and 80 were leaking, mainly from pinholes along the longitudinal seam.

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.

Caution must be the keyword in analyzing tetraethyl lead in the laboratory. The following points should be observed (Ethyl MSDS 1982):

- All work should be performed in a fume hood.
- Under no circumstances should solutions containing TEL be distilled or heated.
- Skin contact should be avoided and neoprene or vinyl or acid-proof rubber gloves should be worn.
- All glassware should be washed repeatedly in naphtha solvent before returning to service and the solvent disposed of as noted in Chapter 9.
- Gloves and clothing should be disposed of after the procedure is complete.

11.1 Quantitative Method for the Detection of Tetraethyl Lead in Air

11.1.1 Gas Chromatography (NIOSH 1978). A range of 0.045 to 0.20 mg/m^3 (0.003-0.015 ppm) of tetraethyl lead (as lead) in air may be determined using gas chromatography with a photoionization detector.

A known volume of air is drawn through a 10 cm by 6 mm O.D. glass tube containing two sections of 20/50 mesh XAD-2 resin. The front section contains 100 mg and is separated from the backup section containing 50 mg by a piece of silylated glass wool. A sample size of 120 L is recommended at a flow rate of 1.0 L/min.

The sample tube is scored with a file and the 100 mg resin section is transferred to a 2 mL sample vial. The backup section is analyzed separately. A 1.0 mL volume of pentane is transferred to the sample vial and the sample is desorbed for 30 minutes.

A 5 µL aliquot of desorbed sample is injected into a gas chromatograph equipped with a photoionization detector. The tetraethyl lead is determined using an electronic integrator and retention times as well as a standard curve.

Typical gas chromatograph conditions are: nitrogen carrier gas flow at 20 mL/min, injector temperature at 185°C, oven temperature at 200°C, detector temperature at 210°C, and column temperature at 75°C.

11.2 Qualitative Method for the Detection of Tetraethyl Lead in Air

The sample is collected as in Section 11.1.1 and desorbed. A small portion of the desorbed sample is treated with a few drops of 6 M ammonium hydroxide and then treated wilth hydrogen sulphide gas. A brown colouration indicates the presence of a lead compound (Welcher 1955). Alternately, a portion of desorbed sample can be burned in a flame using a platinum wire. An orange-coloured flame with a green margin indicates tetraethyl lead (Merck 1976).

11.3 Quantitative Method for the Detection of Tetraethyl Lead in Water

11.3.1 Atomic Absorption (ASTM 1979). A range of up to 40 ppm of tetraethyl lead in water may be determined by atomic absorption spectrometry. A minimum of 1 L of a representative sample is collected in an appropriate container. A 100 mL volume of sample is combined with 0.5 mL of concentrated nitric acid. A 5 mL volume of concentrated hydrochloric acid is added to the mixture. The sample is evaporated to approximately 20 mL in a fume hood. The sample is cooled and filtered. The filtrate is collected in a 100 mL volumetric flask. The filter should be rinsed a few times and the washing combined in the volumetric flask. The volume is taken to 100 mL with water. The sample is aspirated into a suitable atomic absorption spectrophotometer at a wavelength of 283.3 nm. The absorbance is read and the lead determined using a standard curve. Typical atomic absorption spectrophotometer conditions are: a lead or multi-element hollow cathode lamp, purified air as the oxidant, acetylene as the fuel. A blank or baseline level should be established by aspirating 0.2 percent nitric acid between standard solutions as well as samples.

11.4 Qualitative Method for the Detection of Tetraethyl Lead in Water

The sample is collected as in Section 11.3.1 but without acidification. A few drops of sample are treated with a few drops of ammonium hydroxide and then treated with hydrogen sulphide gas. A brown colouration indicates the presence of a lead compound (Welcher 1955).

Alternately, a small portion of sample can be burned in a bunsen burner flame using a platinum wire. An orange-coloured flame with a green margin indicates the presence of tetraethyl lead (Merck 1976).

11.5 Quantitative Method for the Detection of Tetraethyl Lead in Soil

11.5.1 Spectrophotometric (Hesse 1972). Although this method is specifically for the determination of lead, it may be used for tetraethyl lead. A range of 0 to 1 ppb of lead may be determined in soil by spectrophotometric measurement. The range may be extended by sample dilution.

A 1.0 g sample of 0.15 mm soil is placed in a 250 mL beaker and 20 mL of concentrated nitric acid added. The beaker is covered and heated using low heat. A 10 mL volume of 60 percent perchloric acid is added and the mixture digested until dense white fumes appear. The sides of the beaker are washed with a small amount of perchloric acid. The mixture is digested for 15 minutes to dehydrate the silica, cooled, and diluted with 25 mL of warm water. The mixture is then filtered through a Whatman 41 filter paper and the filtrate collected in a 100 mL volumetric flask. The silica residue is washed with 0.5 M hydrochloric acid and the wash added to the flask. The solution is taken to volume with 0.5 M hydrochloric acid.

A 50 mL aliquot of digest is transferred to a 125 mL separatory funnel. A 5 mL volume of ammonium citrate buffer is added. The buffer is prepared by dissolving 225 g of ammonium citrate in 1 L of water. The pH of the buffer is adjusted to 8.5 with 40 mL of strong ammonium hydroxide solution. The mixture is extracted with 20 mL portions of dithizone in carbon tetrachloride.

Dithizone in carbon tetrachloride is prepared by dissolving 0.25 g of diphenylthiocarbazone in 1 L of pure carbon tetrachloride. A 2 mL volume of 0.02 M ammonium hydroxide is added and the mixture shaken for 5 minutes. The carbon tetrachloride layer is discarded and the solution is extracted with 50 mL portions of pure carbon tetrachloride until the extract is clear green. A 500 mL volume of carbon tetrachloride and 50 mL of 1.0 M hydrochloric acid are added and the mixture shaken. The aqueous layer is discarded and the organic layer is diluted to 2 L. A 25 mL volume of water partly saturated with sulphur dioxide is added. The prepared dithizone in carbon tetrachloride is stored in an amber bottle.

The ammonium citrate buffer preparation is continued in the following manner. The pH-adjusted buffer is extracted with more 20 mL portions of dithizone in carbon tetrachloride until the organic phase remains green and the aqueous phase remains orange. The aqueous phase is extracted with pure carbon tetrachloride and a suitable volume of ammonium hydroxide is used to adjust the pH to 2.5.

The sample (digest) treatment is continued in the following manner. A 5 mL volume of dithizone solution is added and the mixture shaken for 5 minutes. The dithizone phase is discarded. The aqueous phase is extracted with another 5 mL portion of dithizone and the dithizone phase discarded.

A 5 mL volume of citrate buffer is added to the aqueous phase and, if necessary, the pH is adjusted to 8.5 with ammonium hydroxide. A 10 mL volume of dithizone solution is added and the mixture shaken for 2 minutes. The dithizone phase is run into a clean funnel and the aqueous phase re-extracted until the extract is green. The extracts are combined with the dithizone phase in the clean funnel and the aqueous phase kept in the funnel. A 25 mL volume of 0.02 M hydrochloric acid is added to the combined dithizone extracts and the mixture shaken for 2 minutes. The dithizone phase is discarded and the aqueous phase combined with the aqueous phase kept in the funnel.

To the combined aqueous extracts, 10 mL dithizone solution, 5 mL ammonium citrate buffer, 10 mL 10 percent potassium cyanide and sufficient ammonium hydroxide to obtain a pH of 9.3 are added. The mixture is shaken for 3 minutes. The carbon tetrachloride phase is transferred to a clean separatory funnel, washed with 50 mL of 0.01 M ammonium hydroxide solution, and filtered through a cotton wool plug into a suitable spectrophotometer cell. The absorbance of the sample is measured at 520 nm. The sample concentration is determined by a standard curve covering the range 0-1 µg/mL lead and a reagent blank must be measured.

11.6 Qualitative Method for the Detection of Tetraethyl Lead in Soil

The sample is digested as in Section 11.5.1. A small portion of sample is burned in a bunsen burner flame using a platinum wire. An orange-coloured flame with a green margin indicates tetraethyl lead (Merck 1976).

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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 immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre

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