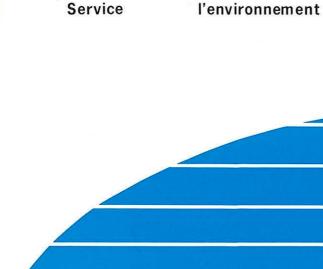


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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

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

ETHYLBENZENE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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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 draft of this manual was prepared under a contract with Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited. The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The Canadian Chemical Producers' Association is especially acknowledged for its review of and input to this manual. The final version was prepared by the staff of the Environmental Protection Service who rewrote the text, drafted illustrations and incorporated all comments and additions. TABLE OF CONTENTS

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I SUMMARY

ETHYLBENZENE (C6H5C2H5)

Colourless liquid with a sweet, gasoline-like odour

SYNONYMS

Phenylethane, Ethylbenzol, EB

IDENTIFICATION NUMBERS

UN No. 1175; STCC 4909163; CAS No. 100-41-4; OHM-TADS No. 7216709

GRADES & PURITIES

Technical, 99 percent minimum

IMMEDIATE CONCERNS

Fire: Flammable liquid, vapours form explosive mixtures in air at concentrations of 1.0 to 6.7 percent

Human Health: Moderately toxic by inhalation, contact and ingestion

Environment: Harmful to some species of aquatic life at concentrations as low as 0.4 mg/L

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): liquid Boiling Point: 136.2°C Flammability: flammable Flash Point: 15°C (CC) Vapour Pressure: 1.3 kPa @ 25°C Specific Gravity (water=1): 0.867 @ 20°C Solubility (in water): 0.015 g/100 mL @ 20°C Behaviour (in water): floats, with no reaction Behaviour (in air): vapours are heavier than air and form explosive mixtures with air Odour Threshold (in water): 0.2 to 140 ppm Odour Threshold (in air): 0.25 ppm

ENVIRONMENTAL CONCERNS

An ethylbenzene slick could pose an immediate hazard to waterfowl and marine animals. It is harmful to aquatic life in low concentrations, but has not been shown to be bioaccumulative or bioconcentrative.

HUMAN HEALTH

TLV*: 100 ppm (435 mg/m³) IDLH: 2,000 ppm (8,700 mg/m³)

Exposure Effects

Inhalation: If inhaled, causes irritation of mucous membranes, dizziness, headache, and depression of the central nervous system

Contact: Contact with liquid causes irritation to eyes and skin

IMMEDIATE ACTION

Spill Control

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

Fire Control

Do not extinguish fire unless release can be stopped. Use foam, dry chemical or carbon dioxide to extinguish. Water sprays may be used on large fires. Cool fire-exposed containers with water. Stay clear of ends of tanks.

COUNTERMEASURES

Emergency Control Procedures in/on

- Soil: Construct barriers to contain spill or divert to impermeable surfaces. Remove material with pumps or vacuum equipment. Absorb residuals with sand or synthetic sorbents, shovel into containers which can be covered
- Water: Contain with booms, weirs or natural barriers. Use (oil) skimming equipment to remove slick, followed by the application of sorbents
- Air: Use water spray to knock down and disperse flammable vapour. Control runoff for later treatment and/or disposal

NAS HAZARD RATING

Category	Rating	
Fire	3	
Health Vapour Irritant Liquid or Solid Irritant Poisons	2	NFPA HAZARD CLASSIFICATION
Water Pollution Human Toxicity Aquatic Toxicity Aesthetic Effect	3	Flammability
Reactivity Other Chemicals Water Self-reaction	0	Health 2 0 Reactivity

3

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance

Usual shipping state Physical state at 15°C, 1 atm Melting point Freezing point Boiling point

Vapour pressure

Densities

Specific gravity (water = 1)

Vapour density (air = 1)

Fire Properties

Flammability

Flash point CC

Autoignition temperature Burning rate

Upper flammability limit

Lower flammability limit Upper explosive limit

Lower explosive limit Flame speed

Heat of combustion Flashback potential

Electrical ignition hazard

Other Properties

Molecular weight of pure substance

Colourless liquid (CCD 1978) Liquid (Sun Petroleum MSDS 1981) Liquid (Merck 1976) -94.97°C (CRC 1980) -95°C (Dow ERIS 1980) 136 to 137°C (Sun Petroleum MSDS 1981) 136.2°C (CRC 1980); 136°C (CCPA 1982) 1.3 kPa (25°C) (Perry 1973) 2.6 kPa (38.6°C) (AWQC 1980)

0.8670 (20°/4°C) (CRC 1980) 0.865 (25°/25°C) (CCPA 1982)

3.66 (Verschueren 1977)

Flammable liquid; vapours form explosive mixtures with air (NFPA 1978)

15°C (NFPA 1978); 21°C (CCPA 1982) 27°C (CHRIS 1978)

432°C (NFPA 1978)

5.8 mm/min (CHRIS 1978)

6.7% (v/v) (NFPA 1978)

1.0% (v/v) (NFPA 1978)

6.7% (v/v) (Sun Petroleum MSDS 1981)

1.0% (v/v) (Sun Petroleum MSDS 1981)

0.35 m/s (maximum when burning in air) (Lange's Handbook 1979)

4564.9 kJ/mole (Sussex 1977)

Vapour may travel considerable distance to a source of ignition and flashback (NFPA 1978)

May be ignited by static discharge

106.17 (CRC 1980)

Constituent components (percent) (of typical commercial grade)

Refractive index Viscosity

Liquid interfacial tension with air Liquid interfacial tension with water Latent heat of fusion Latent heat of sublimation Latent heat of vaporization Heat of formation

Ionization potential Heat capacity constant pressure (Cp)

constant volume (Cv)

Critical temperature343.9°C (CRC 1980)Critical pressure3,740 kPa (CRC 1980)Coefficient of thermal expansion (volume)0.0009/°C (Lange's Handbook 1979)Thermal conductivity1.32 mJ•cm/(s•cm2•°C) (25°C) (CRDiffusivity (gas)0.0658 cm²/s (in air at 0°C) (Perry

Saturation concentration

Evaporation rate

Log10 Octanol/water partition coefficient 3.15 (Chiou and Schmedding 1982)

Solubility (g/100 mL)

In water

In other common materials

4

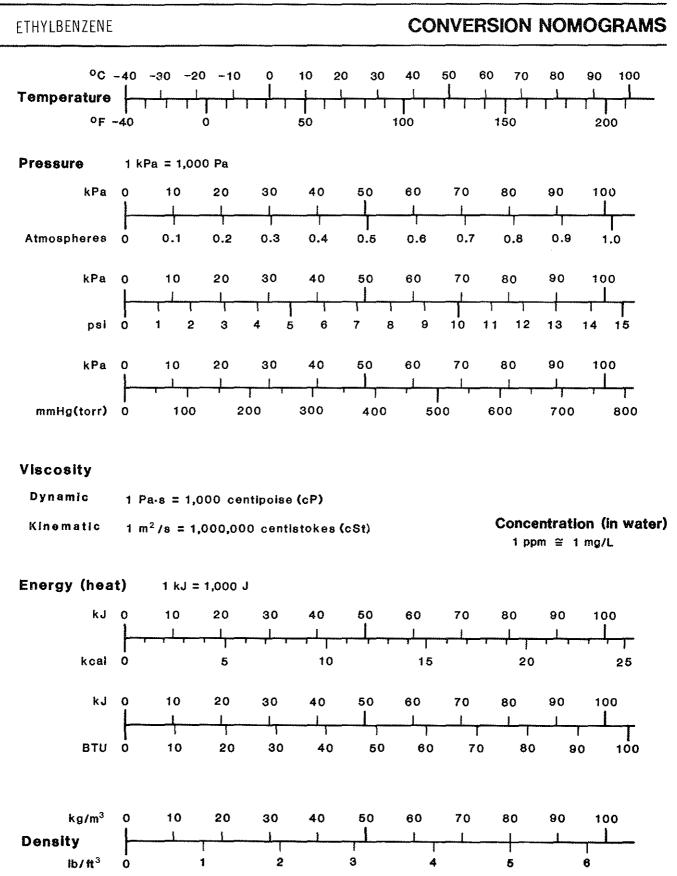
99.7 percent ethylbenzene, 0.1 percent μ- and p-xylene, 0.1 percent cumene and 0.1 percent toluene (Sun Petroleum MSDS 1981)
1.4959 (20°C) (CRC 1980)
0.678 mPa•s (20°C) (Lange's Handbook 1979)
0.691 mPa•s (17°C) (CRC 1980)
0.029 N/m (20°C) (CRC 1980)
0.035 N/m (20°C) (CRC 1980)
0.035 N/m (20°C) (CHRIS 1978)
9.15 kJ/mole (Perry 1973)
42.2 kJ/mole (25°C) (Lange's Handbook 1979)
42.3 kJ/mole (25°C) (Sussex 1977)
Liquid: -13.1 kJ/mole (Sussex 1977)
8.76 eV (Rosenstock 1977)
Liquid: 1.75 J/(g•°C) (25°C) (CRC 1980)

Gas: 1.21 J/(g•°C) (25°C) (CRC 1980) Gas: 1.13 J/(g•°C) (25°C) (CRC 1980) (CHRIS 1978) 343.9°C (CRC 1980) 3,740 kPa (CRC 1980) 0.0009/°C (Lange's Handbook 1979) 1.32 mJ•cm/(s•cm²•°C) (25°C) (CRC 1980) 0.0658 cm²/s (in air at 0°C) (Perry 1973) 0.077 cm²/s (in air at 25°C) (Thibodeaux 1979) 40 g/m³ (20°C) (Verschueren 1977) 67 g/m³ (30°C) (Verschueren 1977) 0.27 g/(m²•s) (20°C) (see Section 5.3.2.1) 3.15 (Chiou and Schmedding 1982)

0.015 (20°C) (GE 1978) 0.014 (25°C) (CCPA 1982)

Miscible in ethanol and diethyl ether (CRC 1980); soluble in benzene and carbon tetrachloride (CCD 1978)

TABLE 1





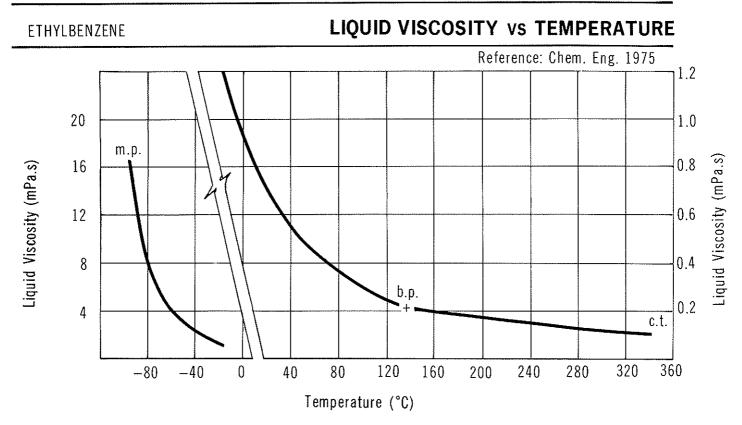
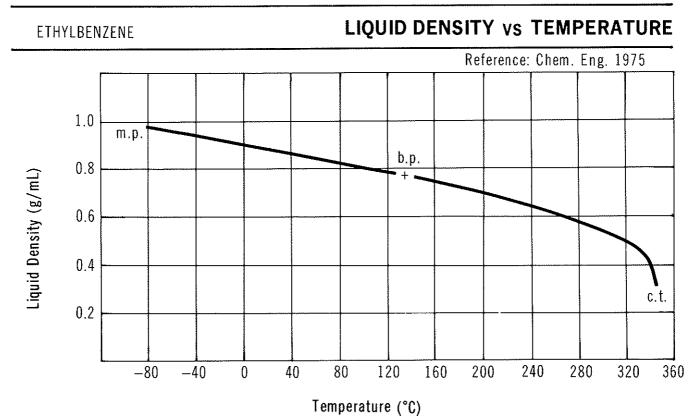


FIGURE 2



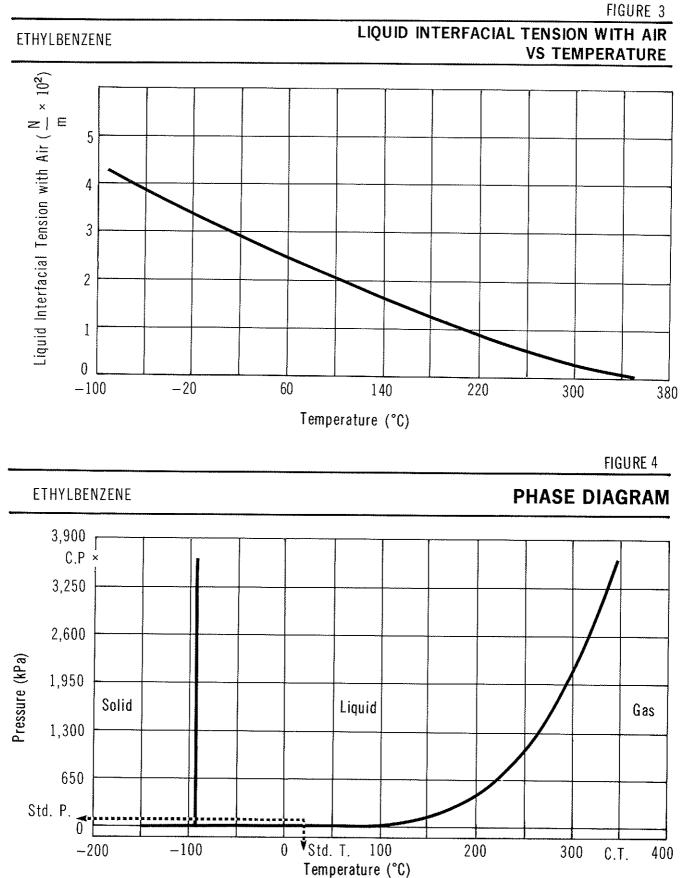
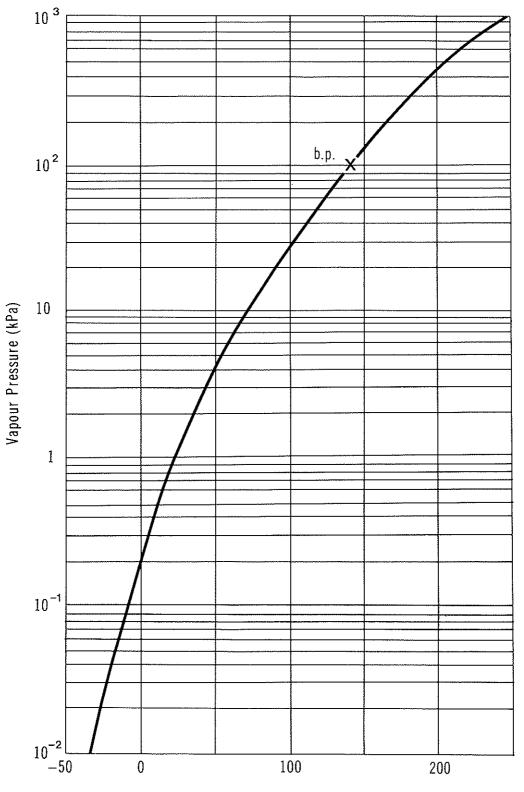


FIGURE 5 VAPOUR PRESSURE VS TEMPERATURE

Reference : Chem. Eng. 1975



Temperature (°C)

ETHYLBENZENE

3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Dow PS 1980)

Ethylbenzene is produced in technical grade (99.0 percent).

3.2 Domestic Manufacturers (Corpus 1981; CBG 1980)

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

Dow Chemical Canada Inc. Box 1012 Modeland Road Sarnia, Ontario N7T 7K7 (519) 339-3131 Polysar Limited 201 Front Street North Sarnia, Ontario N7T 7V1 (519) 332-1212

3.3 Major Transportation Routes

Current Canadian production of ethylbenzene is all in the Sarnia area. Because its major use, the manufacture of styrene, also takes place only in Sarnia, bulk transportation (by rail car) occurs only over the short distance between manufacturers' plants.

3.4 Production Levels (Corpus 1981; PC; Finachem PDS 1981)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1981)
Dow Chemical Canada, Sarnia, Ontario		91
Polysar, Sarnia, Ontario*		444
	TOTAL	535
Domestic Shipments (1980)		338.0
Imports (1980)		0.5
	TOTAL	338.5

* Primarily for captive use.

3.5 Future Development (Finachem PDS 1981)

Two ethylbenzene plants are being proposed for Alberta. Nova and Shell Canada plan to build a 345 kt/yr plant at Scotford. Petalta plans to construct a 460 kt/yr plant at Bruderheim. If approved, these plants, located near Edmonton, will come onstream in 1984.

3.6 Manufacture of Ethylbenzene (Noller 1958)

3.6.1 General. Ethylbenzene is manufactured in Canada by the Friedel-Crafts alkylation of benzene with ethylene.

3.6.2 Manufacturing Process. Benzene vapour, present in excess, and ethylene are mixed and passed through a liquid aluminum chloride/hydrogen chloride/hydrocarbon complex catalyst.

C₆H₆ + C₂H₄ $\xrightarrow{A1C1_3-HC1}$ C₆H₅C₂H₅ benzene ethylene 95°C, 35 kPa ethylbenzene

The product is purified by distillation; unreacted benzene and higher-alkylated benzenes are recycled to give better yields. Yields greater than 95 percent based on ethylene or benzene can be obtained.

3.7 Major Uses in Canada (Corpus 1981; Dow PS 1980)

Ethylbenzene is used for the production of styrene and as a solvent in the chemical, paint, and rubber industries.

3.8 Major Buyers in Canada (Corpus 1981)

Dow Chemical Canada, Sarnia, Ontario.

11

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

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

4.1.1.1 Railway tank cars. Railway tank cars used to transport ethylbenzene are classified under the A-8 Class CTC IIIA tank specification. Each specification is described in Table 2 (TCM 1979).

TABLE 2RAILWAY TANK CAR SPECIFICATIONS

DOT* and CTC** Specification Number	Description
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A60F1	Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A100W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Bottom outlet or washout optional. Test pressure 690 kPa (100 psi).

* Department of Transportation (U.S.)

** Canadian Transport Commission

Ethylbenzene is usually shipped in railway tank cars with capacities of 30,400 L (6,700 Imp. gal.), 37,700 L (8,300 Imp. gal.), 60,400 L (13,300 Imp. gal.), and 75,700 L (16,700 Imp. gal.). Figure 6 shows a Class 111A60W1 railway car used to transport ethylbenzene; Table 3 indicates railway tank car details associated with this drawing (TCM 1979). Cars are equipped for unloading by pump or gravity through either one of two 152 mm (6 in.) diameter bottom outlets provided with inner plug valves. In

ETHYLBENZENE

RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979, RTDCR 1974)

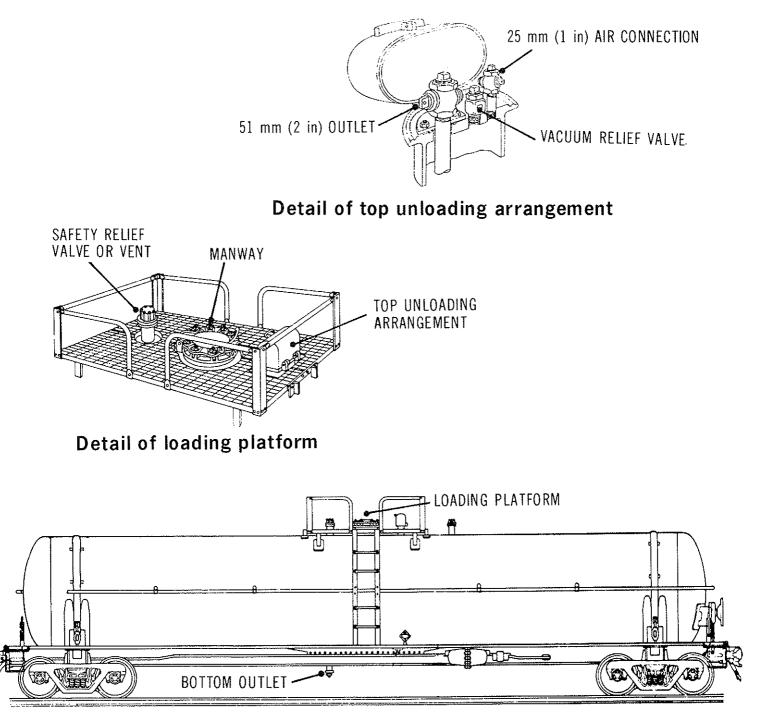


Illustration of tank car layout

TABLE 3	TYPICAL RAILWAY TANK CAR SPECIFICATIONS -	- CLASS 111A60W1 (TCM 1979: RTDCR 19) 74)
	I TEICAL KALWAT TANK CAR SPECIFICATIONS -	- CLASS IIIA60WI (ICM 1979; RIDCR I	27

Descuintian	Tank Car Size (Imp. Gal.)				
Description Overall	16,700	17,200	20,000		
Nominal capacity Car weight- empty Car weight- (max.)	75,700 L (16,700 gal.) 33,900 kg (74,700 lb.) 119,000 kg (262,000 lb.)	78,000 L (17,200 gal.) 33,900 kg (74,700 lb.) 83,500 kg (184,000 lb.)	90,900 L (20,000 gal.) 38,900 kg (85,800 lb.) 119,000 kg (262,000 lb.)		
Tank					
Material Thickness Inside diameter Test pressure Burst pressure	Steel 11.1 mm (7/16 in.) 2.60 m (102 in.) 414 kPa (60 psi) 1,640 kPa (238 psi)	Steel 11.1 mm (7/16 in.) 2.62 m (103 in.) 414 kPa (60 psi) 1,640 kPa (238 psi)	Steel 11.1 mm (7/16 in.) 2.74 (108 in.) 414 kPa (60 psi) 1,640 kPa (238 psi)		
Approximate Dimensions	•	•			
Coupled length Length over strikers Length of truck centres Height to top of grating Overall height Overall width (over grabs) Length of grating Width of grating	17 m (56 ft) 16 m (52 ft) 13 m (43 ft) 4 m (13 ft) 5 m (16 ft) 3.2 m (126 in.) 2-3 m (7-10 ft) 1.5-2 m (5-7 ft)	17 m (56 ft) 16 m (52 ft) 13 m (43 ft) 4 m (13 ft) 5 m (16 ft) 3.2 m (126 in.) 2-3 m (7-10 ft) 1.5-2 m (5-7 ft)	18 m (59 ft) 17 m (56 ft) 14 m (46 ft) 4 m (13 ft) 5 m (16 ft) 3.2 m (126 in.) 2-3 m (7-10 ft) 1.5-2 m (5-7 ft)		
Loading/Unloading Fixtures					
<u>Top Unloading</u> Unloading connection Manway/fill hole Air connection	51 mm (2 in.) 203-356 mm (8-14 in.) 25-51 mm (1-2 in.)	51 mm (2 in.) 203–356 mm (8–14 in.) 25–51 mm (1–2 in.)	51 mm (2 in.) 203-356 mm (8-14 in.) 25-51 mm (1-2 in.)		
Bottom Unloading Bottom outlet	102 152	102 152	102,152 (4,4,5)		
Safety Devices	102-152 mm (4-6 in.) Safety vent or valve	102-152 mm (4-6 in.)	102-152 mm (4-6 in.)		
Dome	None				
Insulation	Optional				

ξ

addition to bottom unloading, the cars may be unloaded from the top by pump. In this case, the ethylbenzene is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with an unloading connection valve. Air pressure is never used for unloading ethylbenzene.

A safety relief valve set at 241 kPa (40 psi) is required on top of the rail car. A gauging device, either the rod type or the tape type, is optional. The top unloading connection must be protected by a housing cover. The maximum pressure allowable for the CTC IIIA100W1 rail cars is 448 kPa (65 psi) (TCM 1979). When the 111A60W1 or 111A60F1 cars are used, this maximum pressure would be 276 kPa (40 psi). Ethylbenzene is never transported under pressure.

4.1.1.2 Tank motor vehicles and portable tanks. Ethylbenzene is manufactured in Canada for captive use in the production of styrene. Because of this, the chemical is not transported outside the plant boundary by tank motor vehicle or portable tank. The only known method of transportation of ethylbenzene in Canada is by rail car as previously described.

4.1.2 Packaging. In addition to railway bulk shipments, ethylbenzene is also transported in drums (Figure 7). Drums fabricated from a variety of construction materials are permitted as shown in Table 4 (TDGC 1980).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Ethylbenzene Railway Tank Cars. Prior to off-loading, certain precautions must be taken (MCA 1960):

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution placards displayed.
- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- The tank car must be effectively grounded.

Where top off-loading is used, proceed as follows (MCA 1960):

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

ETHYLBENZENE

TYPICAL DRUM CONTAINERS

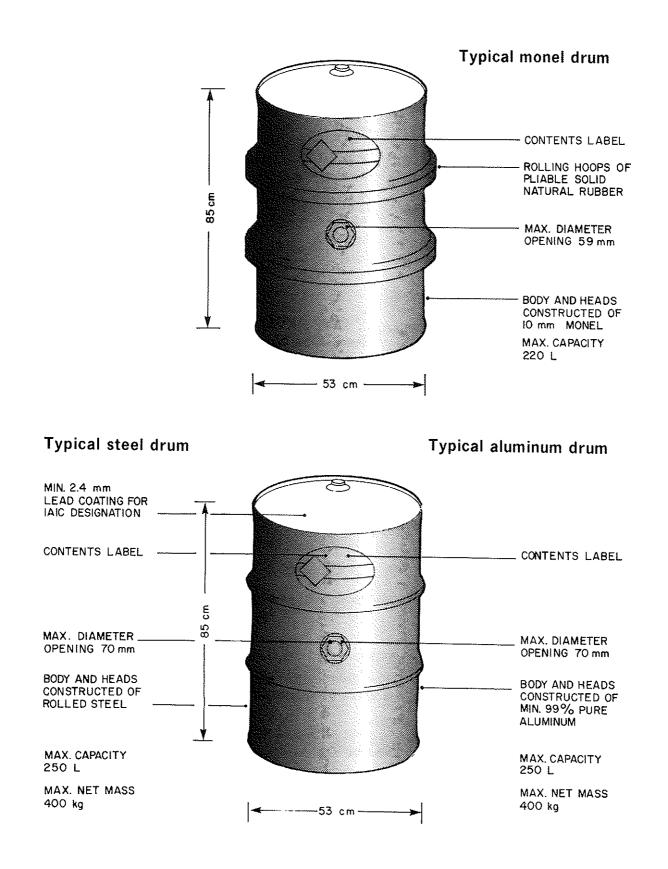


FIGURE 7

Type of Drum	Designation	Description	Figure No. (where (applicable)
Steel	IAI	Nonremovable head, reusable	7
	IAIA	As IA1 with reinforced chime	7
	IAIB	As 1A1 with welded closure flange	7
	IAID	As 1A1 with coating (other than lead)	7
	1A2	Removable head, reusable	7
	1A3	Nonremovable head, single use only	7
Monel (nickel- copper alloy)	TC5M		7
Aluminum	IBI	Nonremovable head	7
	1B2	Removable head	7
Steel Drums with inner plastic receptacles	6HAI	Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity of 225 L	
Fibre Board Drums with inner plastic receptacles	6HGI	Outer containers of con- volutely wound plies of fibre board. Inner plastic in shape of drum. Maximum capacity of 225 L	

TABLE 4 DRUMS FOR ETHYLBENZENE

- Off-load tanker by pumping.

Where bottom off-loading is used, proceed as follows using gravity flow or pumping:

- Relieve internal air pressure as previously mentioned.

- After connecting the unloading line to the 152 mm (6 in.) bottom outlet, open the inside bottom valve by turning the valve rod handle at the top of the car.

- Off-load the car by gravity or pump.

4.2.2 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with

specifications refer to those generally used in ethylbenzene service. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets and pumps.

Schedule 40 seamless ASTM Al06 carbon steel pipes and fittings lined with fluorine rubber are recommended for ethylbenzene lines (GF). Seamless or electric resistance pipe ASTM A53 is also suitable (CCPA 1982). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak after a very short time. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipe-line should be tested with air at pressures from 345 to 518 kPa (50 to 75 psi) and all leaks carefully stopped. If leaks develop in service, the only satisfactory way to repair them is to chip out the bad weld and reweld, or to replace the section of pipe.

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

Flexible steel hose or solid pipe with swivel joints may be used for the flexible sections of the unloading line. Either the ball bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance. Some installations of flexible line are made with standard fittings using a number of threaded elbows. This will give sufficient flexibility but usually costs more to maintain because the threaded fittings leak easily. Flexible bellows-type expansion joints with expansion members of tetrafluoroethylene resin could be used for flexible sections (Dow PPS 1972).

For valving, cast iron diaphragm valves lined with glass are recommended (NACE 1967).

Only Viton should be used as a gasket material at normal temperature ranges.

A single-suction, sealless magnetic drive centrifugal pump with "wet end" material of 316 stainless steel gives good results. Leakage from this type of pump is virtually eliminated. Provision must be made for draining the pump so that repairs can be made safely.

The pump should be equipped with flanges at both suction and discharge openings; screw connections are more subject to leakage and should be avoided.

4.3 Compatibility of Ethylbenzene with Materials of Construction

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

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

TABLE 5COMPATIBILITY OF ETHYLBENZENE WITH MATERIALS OF
CONSTRUCTION

				Material of Construction		
Application		Chemical Conc. Temp.(°C)		Recommended	Conditional	Not Recommended
1.	Pipes and Fittings				CS ASTM Al06	
2.	Valves				CI body, wetted parts: SS 316, nickel CS	
3.	Pumps				SS 316	
4.	Storage				ASTM A-283 Gr. C-steel plate	
5.	Others			POM FPM (GF)	CSM* (GF)	uPVC PE PP NR NBR IIR EPDM CR (GF) CSM (Uniroyal
		100%	24 to 100	Glass (NACE 1967)		
		100%	24	Concrete Wood (NACE 1967)		

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

Abbreviation	Material of Construction
CI	Cast Iron, Austenitic
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Concrete
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
IIR	Isobutylene/Isoprene Rubber (Butyl)
NBR	Acrylonitrile/Butadiene Rubber (Nitrile, Buna N)
NR	Natural Rubber
	Nickel
	Nickel-Copper Alloy (Monel)
PE	Polyethylene
РОМ	Polyoxymethylene
PP	Polypropylene
SS (Followed by Grade)	Stainless Steel
uPVC	Unplasticized Polyvinyl Chloride
	Wood

TABLE 6MATERIALS OF CONSTRUCTION

5 CONTAMINANT TRANSPORT

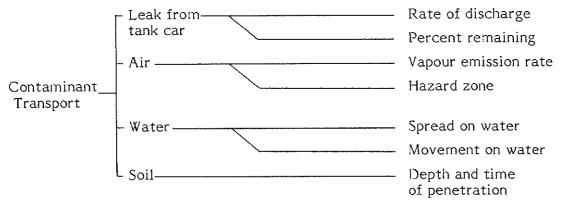
5.1 General Summary

Ethylbenzene is commonly transported in railway tank cars. When spilled in the environment, it will form a liquid pool, spreading on the surface of a water body or on the ground, being adsorbed onto the soil. The vapour is released continuously to the atmosphere by evaporation.

When spilled on water, the slick has a natural tendency to spread. Since it is only slightly soluble and less dense than water, only a very small amount will be dissolved in the water, the rest evaporating to the atmosphere until it is removed.

Ethylbenzene when spilled on the ground is gradually adsorbed onto the soil, at a rate dependent on the soil type and its degree of saturation with water. At the same time, the downward transport of the liquid toward the groundwater table may cause environmental concerns.

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



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

5.2 Leak Nomograms

5.2.1 Introduction. Ethylbenzene is commonly transported in railway tank cars as a non-pressurized liquid. While the capacities of the tank cars vary widely (refer to sub-

section 4.1.1.1), one tank car size has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of 75,700 L (for calculation simplicity, this will be rounded to 80,000 L).

If a tank car loaded with ethylbenzene 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 ethylbenzene 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.

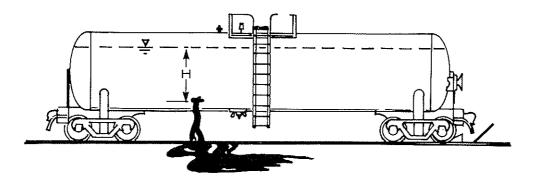


FIGURE 8 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

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

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

5.2.2 Nomograms.

5.2.2.1 Figure 9: Percent remaining versus time. Figure 9 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of

puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car (2.75 m ϕ x 13.4 m long) is assumed to be initially full (at t=0) with a volume of about 80,000 L of ethylbenzene. 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 10: Discharge rate versus time. Figure 10 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture, for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80,000 L.

5.2.3 Sample Calculations.

i) <u>Problem A</u>

The standard tank car (2.75 m ϕ x 13.4 m long), filled with ethylbenzene, 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 9
- . With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28,800 L

ii) Problem B

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

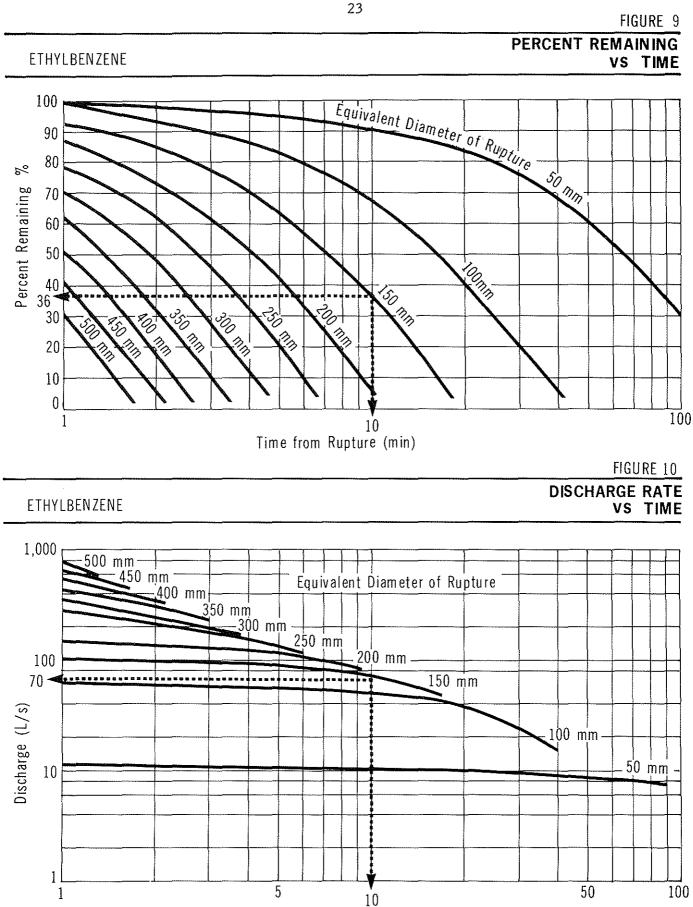
Solution to Problem B

- . Use Figure 10
- . With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 65 L/s

5.3 Dispersion in the Air

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

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and



Time from Rupture (min)

dispersion of the contaminant vapour must be modelled. The models used 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 11 depicts 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 13: vapour emission rate from a liquid pool as a function of maximum pool radius

Table 7: weather conditions

Figure 14: normalized vapour concentration as a function of downwind distance and weather conditions

Table 8: maximum plume hazard half-widths

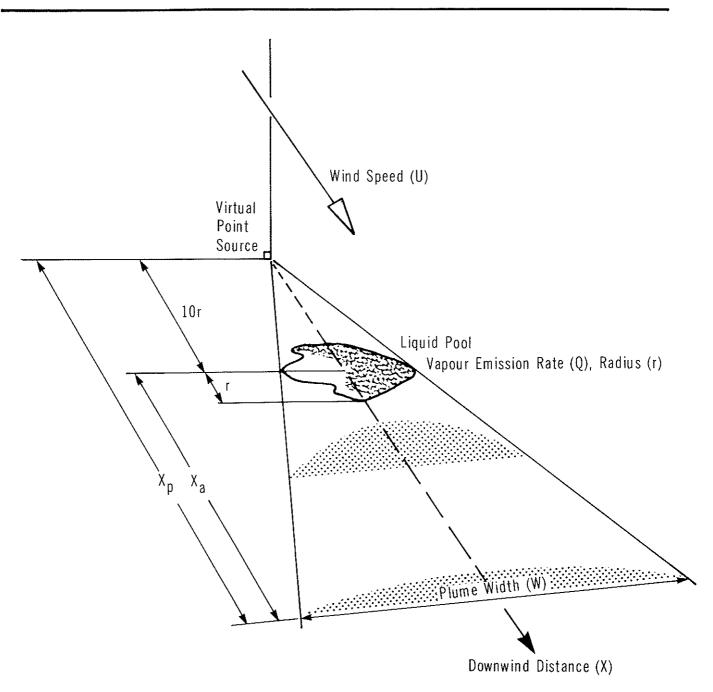
Figure 17: vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flow chart given in Figure 12 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 13: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for ethylbenzene has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for ethylbenzene at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 0.27 g/(m²·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 (Chem. Eng. 1975) of ethylbenzene at that temperature. For example, evaporation rates of 0.069 g/(m²·s) at 0°C and 0.487 g/(m²·s) at 30°C were calculated for a wind speed of 4.5 m/s.

ETHYLBENZENE

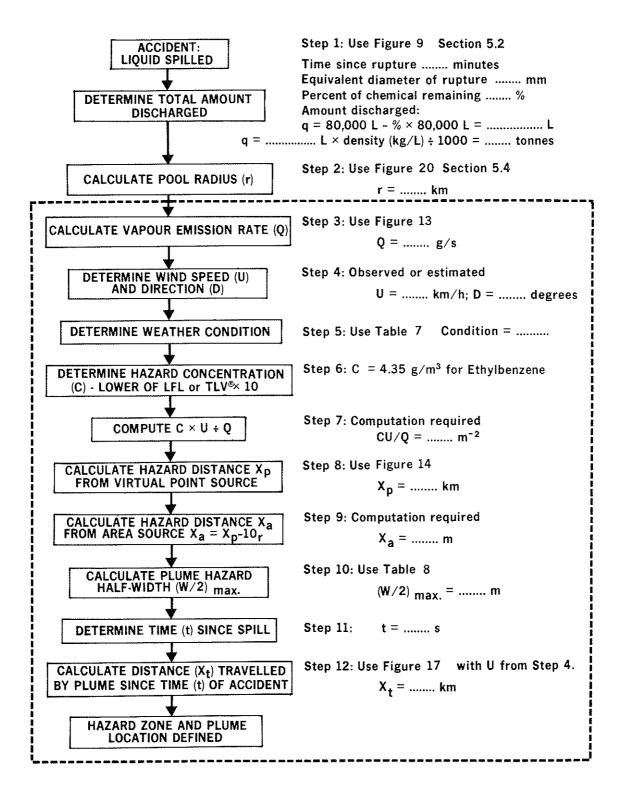
SCHEMATIC OF CONTAMINANT PLUME

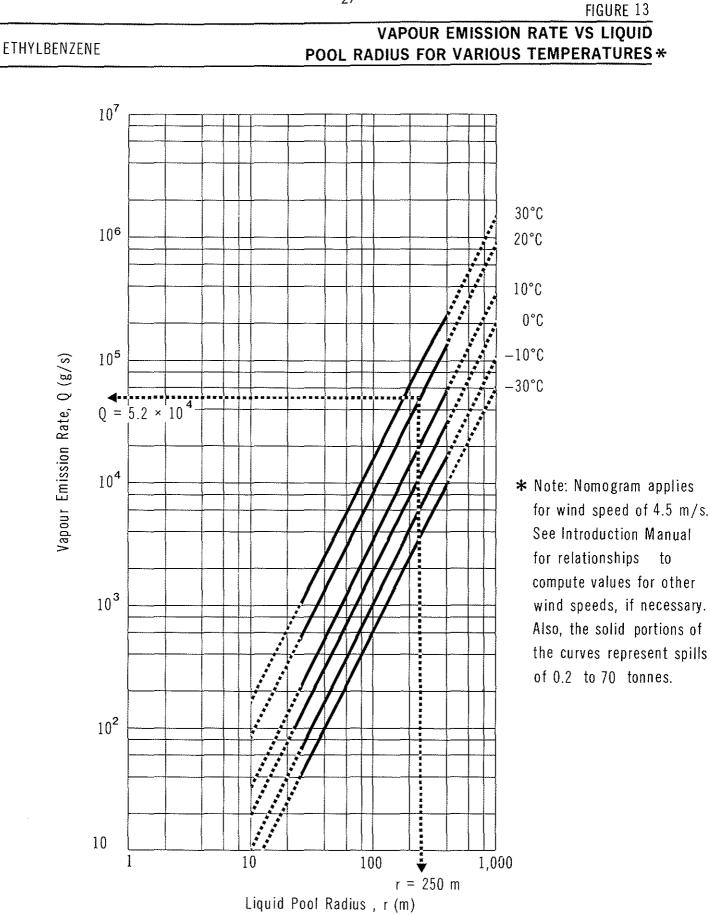


ETHYLBENZENE

FIGURE 12

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE





Using Figure 20, Section 5.4, the maximum spill radius corresponding to various spill amounts of ethylbenzene may be determined. The resultant spill areas and the ethylbenzene evaporation rates provide the basis for preparation of the vapour release rate versus spill radius nomogram in Figure 13.

Use: For a pool of ethylbenzene of known radius, the rate (Q) at which ethylbenzene vapour is released to the atmosphere at a given temperature can be estimated from Figure 13. The solid portions of the curves represent spills of 0.2 to 70 tonnes, the latter representing about one standard 80,000 L rail car load of ethylbenzene. It should be noted that Figure 13 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 ethylbenzene 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.

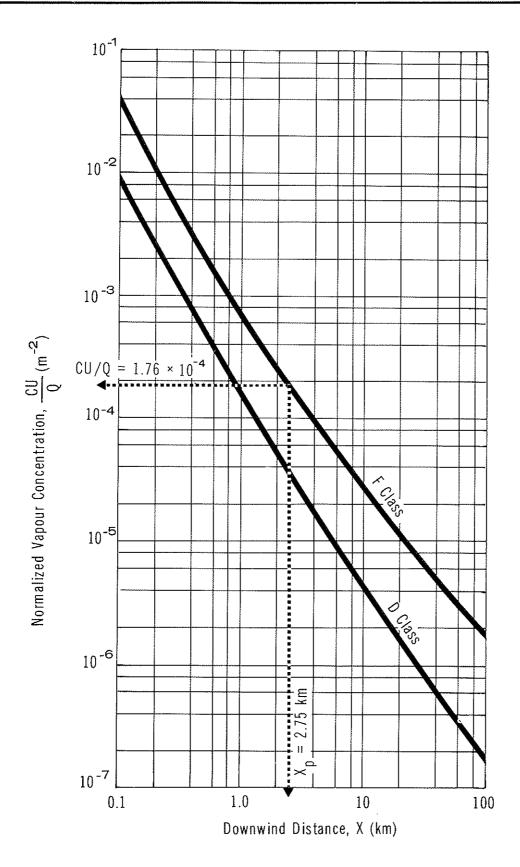
It should also be noted that the determination of the evaporation rate is based on the spill radius on calm water (Table T1, CHRIS 1974). Since calm water represents a flat, unbounded surface compared to the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous), the spill radius on calm water is considered to provide the maximum value. Therefore, when spills on land are assessed by using the water algorithm, the spill radius would be overestimated and worst case values are provided.

5.3.2.2 Figure 14: Normalized vapour concentration versus downwind distance. Figure 14 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 14, the weather condition must be determined from Table 7.

Use: The maximum hazard distance, X_p, downwind of the spill can be calculated from Figure 14 knowing:

- . Q, the vapour emission rate (g/s),
- . U, the wind speed (m/s),
- . the weather condition,
- . the hazard concentration limit, C, which is the lower value of 10 times the Thres-

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



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. .

ETHYLBENZENE

TABLE 7WEATHER CONDITIONS

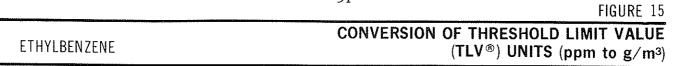
Weather Condition F	Weather Condition D
Wind speed <11 km/h (~3 m/s) and one of the following:	Most other weather conditions
- overcast day	
- night time	
- severe temperature inversion	

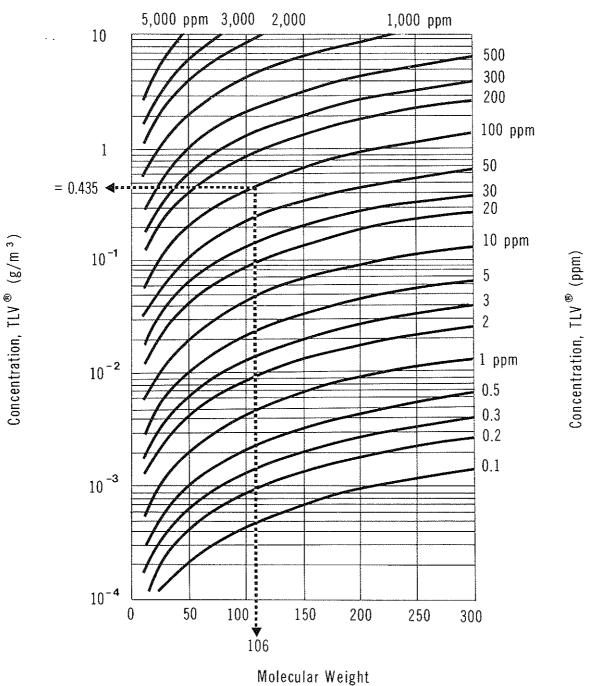
hold Limit Value[®] (TLV[®] in g/m^3) or the Lower Flammability Limit (LFL in g/m^3). Note: To convert the TLV[®] (in ppm) and the LFL (in percent by volume) to concentrations in g/m^3 , use Figures 15 and 16.

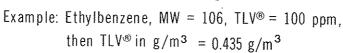
A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e. on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure and use of this value as the hazard limit would result in unrealistically large hazard zones.

5.3.2.3 Table 8: Maximum plume hazard half-widths. This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the ethylbenzene Threshold Limit Value (TLV*) of 0.435 g/m³, or 4.35 g/m³. The maximum plume hazard half-width represents the maximum half-width of the ethylbenzene vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV*. Table 8 is therefore only applicable for an ethylbenzene hazard concentration limit of 10 x TLV* or 4.35 g/m³. Also, data are provided up to a maximum hazard distance downwind (Xp) 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 30,000 to 30,000,000 g/s, corresponding to ethylbenzene spills in the range of about 10 to 5,000 tonnes, respectively. If the entire contents of an 80,000 L (17,600 Imp. gal.) tank car spills, the mass spilled would be 69,400 kg, or approximately 69 tonnes. Therefore, under Class D of Table 8, data are provided for up to 70 times this amount.

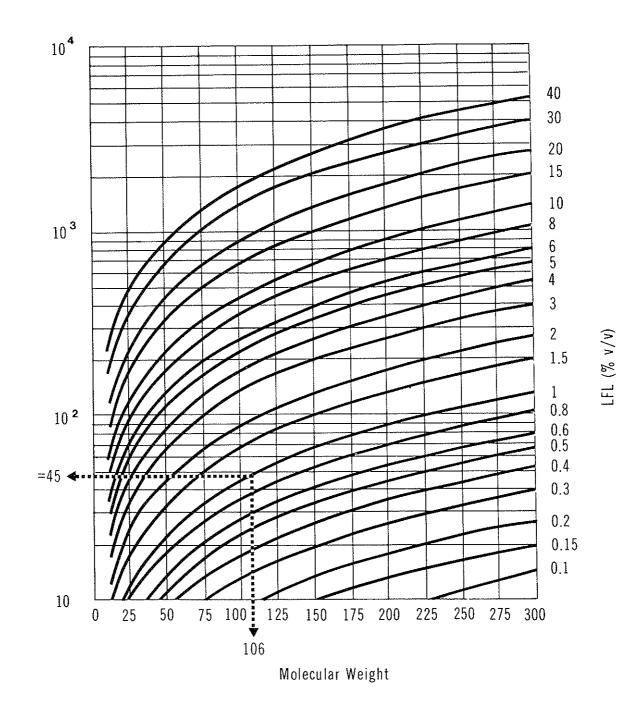






Note: data applicable at 25°C and 760 mm Hg pressure

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





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

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ETHYLBENZENE

Concentration, LFL (g/m 3)

Weather Condition D			Weather Co	ndition F	
Q/U (g/m)	(W/2) _{max} (m)		Q/U (g/m)	(W/2) _{m;} (m)	ax
30,000,000	3,400	(Xp <u><</u> 99.5 km)	2,500,000	1,385	(Xp < 97.4 km)*
25,000,000	3,030		2,000,000	1,175	
20,000,000	2,640		1,500,000	985	
15,000,000	2,210		1,000,000	700	
10,000,000	1,720		750,000	565	
8,000,000	1,500		500,000	420	
6,000,000	1,255		400,000	350	
5,000,000	1,120		300,000	295	
3,000,000	815		250,000	260	
2,500,000	730		200,000	225	
2,000,000	635		150,000	190	
1,500,000	540		100,000	145	
1,000,000	425		50,000	95	
7 <i>5</i> 0,000	360	Q/U = 24,760 →	25,000	60	→ (W/2) _{max} = 60 m
500,000	285		20,000	50	
400,000	250		10,000	35	
300,000	210		5,000	25	
200,000	165		1,000	10	
150,000	140				
100,000	110		* Data are j	provided u	up to a maximum
50,000	75		downwind	hazard d	istance of 100 km;
25,000	50		see page 3	86, step 8	, for sample
10,000	32		calculatio	n.	
5,000	20				
1,000	10				

TABLE 8 MAXIMUM PLUME HAZARD HALF-WIDTHS (for ethylbenzene at 20°C)

<u>Example</u>: A spill releasing ethylbenzene vapour at the rate of $Q = 5.2 \times 10^4$ g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 24,760 g/m which results in a maximum plume hazard half-width (W/2)_{max} = 60 m.

Note: Above table is valid only for an ethylbenzene concentration of 10 x TLV*, or 4.35 g/m^3 .

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 3,000 to 2,500,000 g/s, corresponding to ethylbenzene spills in the range of about 1 to 1,000 tonnes, respectively. Therefore, under Class F of Table 8, data are provided for up to 14 times a standard rail car load.

<u>Use</u>: 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 17: Plume travel time versus travel distance. Figure 17 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.

<u>Use</u>: 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 ethylbenzene. 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 (e.g. of the spill radius) in a particular spill situation if possible.

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

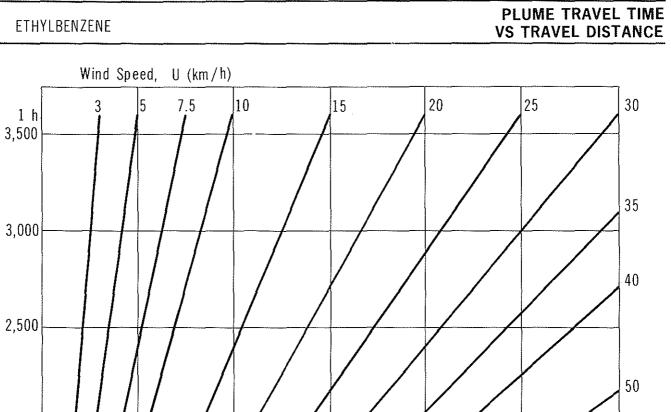
Solution

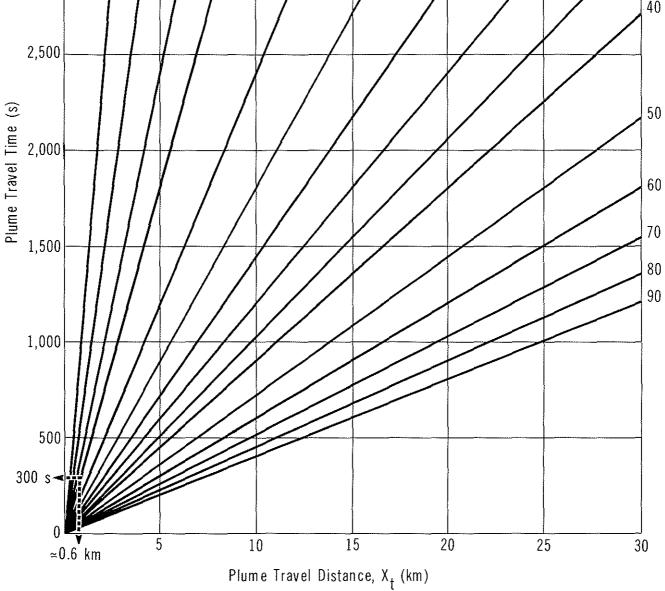
Step 1: Quantity spilled is given, 20 tonnes

Step 2: Calculate pool radius (r) for spill of 20 tonnes

- Use observed (measured) pool radius if possible. If not, use the maximum radius from Figure 20, Section 5.4. Note that use of these data, which apply specifically to spills on water, will result in an exaggerated pool radius on land
- Radius (r) = 250 m ÷ 1,000 = 0.25 km







36 Step 3: Calculate vapour emission rate (Q) at T = 20 °C From Figure 13, r = 250 m and T = 20°C $Q = 5.2 \times 10^4 \text{ g/s}$ Determine wind speed (U) and direction (D) Step 4: Use available weather information, preferably on-site observations For example: U = 7.5 km/h, then $U = 7.5 \div 3.6 = 2.1 \text{ m/s}$ D = NW or 315° (D = Direction from which wind is blowing) Step 5: Determine weather condition From Table 7, weather condition = F since U <11 km/h and it is night Determine hazard concentration limit (C) Step 6: This is the lower of 10 times the TLV® or LFL, so for ethylbenzene $C = 4.35 \text{ g/m}^3 (\text{TLV} = 0.435 \text{ g/m}^3; \text{LFL} = 43.5 \text{ g/m}^3)$ Compute CU/Q . $CU/Q = \frac{4.35 \times 2.1}{5.2 \times 10^4} = 1.76 \times 10^{-4} \text{ m}^{-2}$ Step 7: Calculate downwind hazard distance (X_p) from the virtual point source Step 8: From Figure 14 with $CU/Q = 1.76 \times 10^{-4} \text{ m}^{-2}$ and weather condition F, $X_{D} = 2.75 \text{ km}$ Step 9: Calculate hazard distance (Xa) downwind of the area source With $X_p = 2.75$ km and r = 0.25 km then $X_a = X_p - 10 r = 2.75 \text{ km} - 10 (0.25 \text{ km}) = 0.25 \text{ km}$ Calculate plume hazard half-width (W/2)_{max} Step 10: Use Table 8 With Q = 5.2 x 10⁴ g/s and U = 2.1 m/s then Q/U = $\frac{5.2 \times 10^4}{2.1}$ = 24,760 g/m Then for weather condition F, the closest Q/U value is 25,000 g/m which gives $(W/2)_{max} \sim 60 \text{ m}$ Step 11: Determine time since spill $t = 5 \min x 60 = 300 s$ Step 12: Calculate distance travelled (X_t) by vapour plume since time of accident Using Figure 17 with t = 300 s and U = 7.5 km/h, then $X_t = 0.6$ km (more accurately from Ut = $2.1 \text{ m/s} \times 300 \text{ s} = 630 \text{ m} = 0.63 \text{ km}$

Step 13: Map the hazard zone

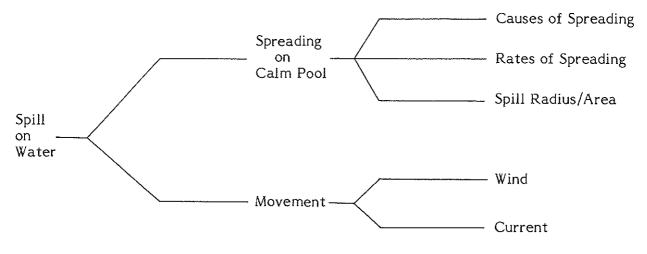
- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (60 m) by the maximum hazard distance downwind of the area source (0.25 km) along the direction of the wind, as shown in Figure 18
- If the wind is reported to be fluctuating by 20° about 315° (or from $315^{\circ} \pm 10^{\circ}$), the hazard zone is shown in Figure 19
- Note that for a wind speed of 7.5 km/h, the ethylbenzene vapour plume will have travelled 0.63 km in the 5 minutes since the spill occurred and that the downwind hazard distance is only 0.25 km

5.4 Behaviour in Water

5.4.1 Introduction. The rate of spreading on water is based on the balance between forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces).

In addition to the natural spreading tendency, the spill slick will move in the same direction and at the same speed as the surface water. Surface water direction and speed are influenced by currents and wind forces.

Factors considered in the spill nomograms are illustrated in the following chart:



HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM



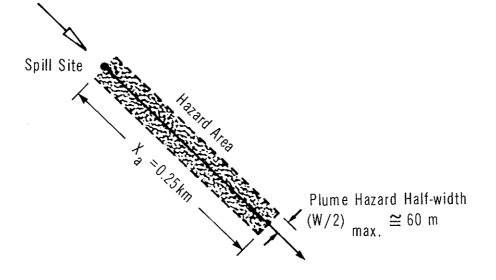
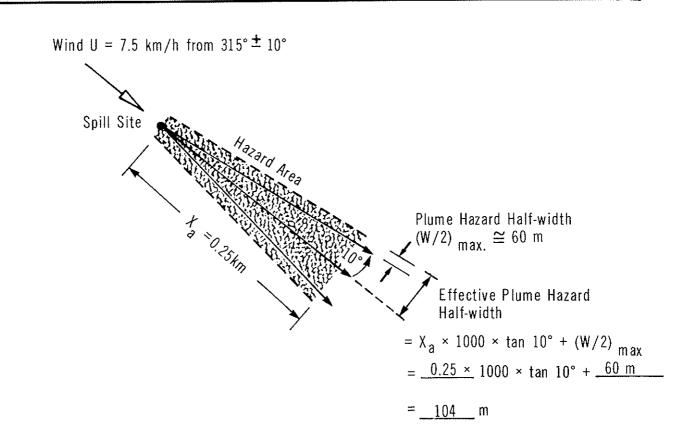


FIGURE 19

ETHYLBENZENE

ETHYLBENZENE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM



- Figure 20: spill radius versus time (still water unconfined) for various sizes of spills; maximum spill radius indicated
- Figure 21: length of channel affected versus equivalent spill radius (still water confined) for a number of stream widths
- Figure 22: translation distance versus time for a range of surface water velocities
- Figure 23: vectoral addition of surface current and wind

5.4.2.1 Figure 20: Spill radius versus time (still water - unconfined). Figure 20 provides a means of calculating the radius/area of an unconfined slick of ethylbenzene for a known mass of spill and at a defined time from the occurrence of the spill. The equations representing the spreading of the spill on water are presented in the Introduction Manual. A critique of the spreading model (Eisenberg 1975) suggests that the equations are valid for cases where the viscosity of the spilled liquid is greater than or equal to 0.2 times the viscosity of water ($U_L > 0.2 U_w$).

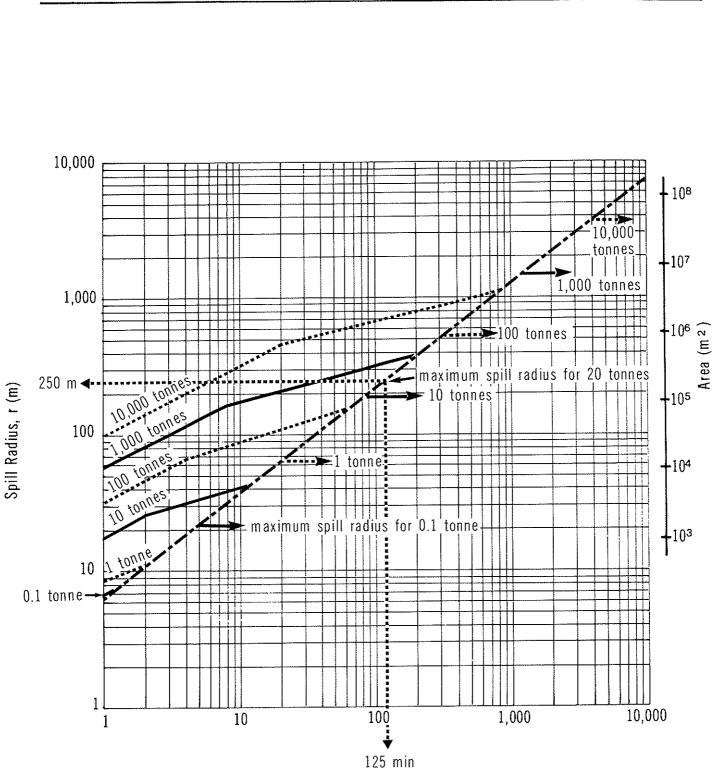
For the purposes of the nomogram presented, the water/spill temperature has been taken at 20°C, representing a reasonable maximum for surface water bodies. This condition maximizes the spill size at any time of interest. If the indicated pool radius is larger than the theoretical maximum radius, use the theoretical maximum pool radius.

5.4.2.2 Figure 21: Length of channel affected versus spill radius (still water - confined). If the distance between the banks of the water body is less than the spill diameter, the slick will be confined. Using the effective radius of spill from Figure 20, the approximate length of channel affected by the spill can be computed from Figure 21, if the stream width (W) is known.

5.4.2.3 Figure 22: Translation distance. Figure 22 presents a simple relationship between velocity, time and distance. The distance a spill will be translated in time by a flowing stream is directly proportional to the surface current.

5.4.2.4 Figure 23: Vectoral addition of surface current and wind. To take into account the effect of both wind and surface current, the spill slick is assumed to move with a velocity given by the vectoral addition of current velocity and 3 percent of the wind velocity (U) (Raj 1974; Fingas 1979, 1980).

Figure 23 is designed to simplify vectoral addition of the current and velocity components. The horizontal velocity axis is scaled for wind velocity, in km/h.



Time (min)

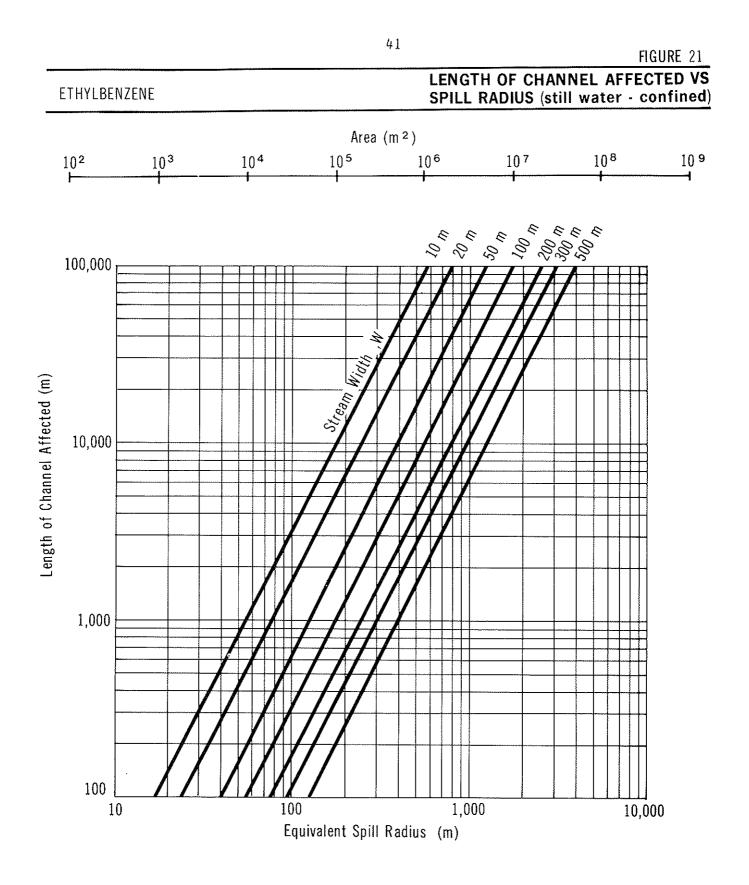
40

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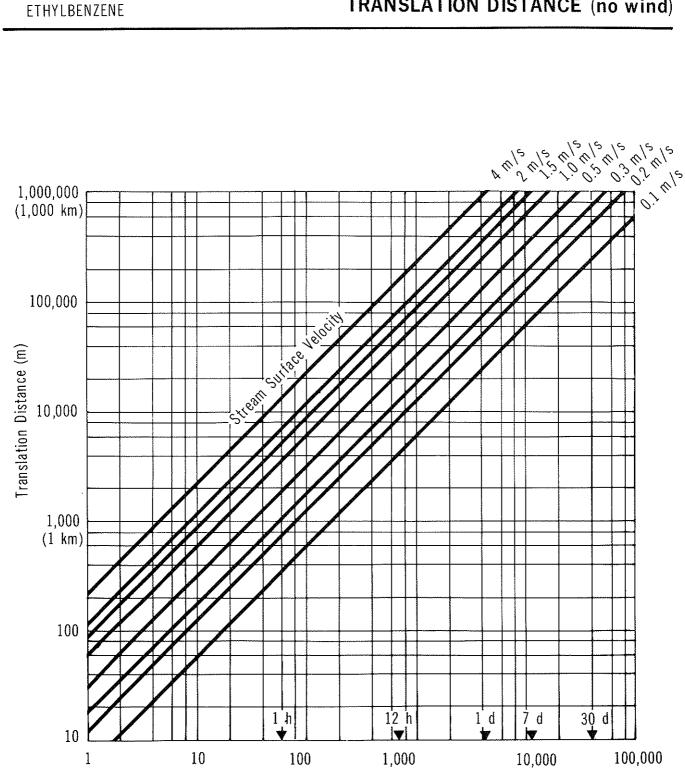
FIGURE 20

SPILL RADIUS VS TIME

(still water - unconfined)







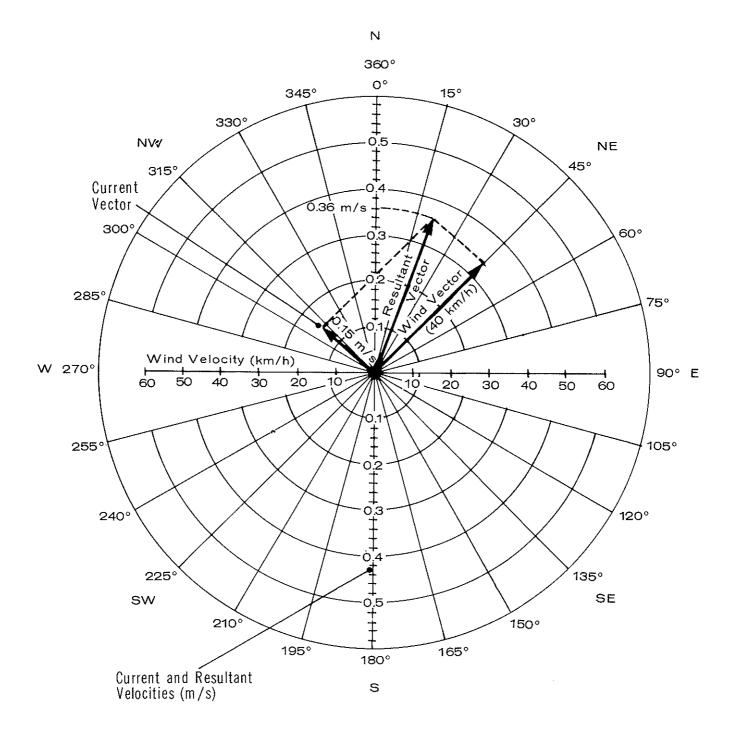
TRANSLATION DISTANCE (no wind)

Time (min)

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VECTORAL ADDITION OF SURFACE CURRENT AND WIND

FIGURE 23



The surface current vector is added to the wind vector by determining its direction relative to the wind direction. The length of the surface current vector is defined by the vertical surface current velocity scale, in m/s.

The resultant vector describes the direction and velocity the spill slick will be moving due to wind and current effects. The length of the resultant vector represents the spill translation velocity (m/s) when measured against the vertical scale.

The nomogram does not account for deformation of the slick shape when influenced by wind and/or surface currents, or for any losses which occur by evaporation or any other means.

5.4.3 Sample Calculations.

i) Problem A

A 20 tonne spill of ethylbenzene has occurred on a large lake. The wind is calm. Determine the size of the spill after 20 minutes, together with the maximum spill size and approximate time of occurrence.

Solution to Problem A

- From Figure 20, with t = 20 min and for a spill mass of 20 tonnes, the spill radius (r) is estimated at about 60 m by interpolation
- . Similarly, the maximum spill radius (r_{max}) of about 250 m will occur in approximately 120 min (2 h)

ii) Problem B

The slick in Problem A is confined to a calm channel approximately 50 m in width. What is the maximum length of channel affected by this spill?

Solution to Problem B

- . Figure 20 (Solution to Problem A) gives $r_{max} = 250$ m for a 20 tonne spill
- . From Figure 21, with $r_{max} = 250$ m and a stream width (W) of 50 m, the maximum length of channel (L) affected under still conditions is about 4,000 m

iii) <u>Problem C</u>

The 20 tonne spill in Problem A is being affected by a wind velocity of 40 km/h from the southwest and a surface current of 0.15 m/s at 90° from the wind direction (i.e. flow is northwest). What is the resultant direction and speed of the slick and the distance the slick has moved when it reaches its maximum size?

Step 1: Define wind vector

- From Figure 23, determine length of wind vector for 40 km/h against horizontal wind velocity scale
- Draw wind vector at appropriate length and in northeasterly direction starting at origin
- Step 2: Define surface current vector
 - From Figure 23, determine length of surface current vector of 0.15 m/s against vertical axis
 - Draw surface current vector at appropriate length and in northwesterly direction, starting from head of wind vector
- Step 3: Define resultant vector
 - Draw resultant vector from origin to head of current vector
 - Direction of translation as given by resultant vector is about 20° east of north
 - Define translation velocity by measuring length of the resultant vector against vertical scale. Spill translation velocity is estimated at 0.36 m/s
- Step 4: Determine distance travelled when spill reaches maximum radius
 - From Figure 20 (or Problem A), $r_{max} = 250$ m at t = 120 min (7,200 seconds)
 - Distance travelled = 7,200 s x 0.36 m/s = 2,600 m, by the time the spill reaches its maximum radius

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Introduction. When ethylbenzene is spilled onto soil and subsequently exposed to precipitation, its transport becomes a multi-phase phenomenon. The phases include the liquids and vapours of ethylbenzene and water, ethylbenzene adsorbed onto soil, and ethylbenzene dissolved in the aqueous phase. However, as described in the Introduction Manual, in spite of this complexity, the central concern with immiscible liquids is downward transport of the liquid toward the groundwater table. The aim of the nomogram developed here is therefore to estimate the rate of penetration of ethylbenzene.

A pattern for the downward movement of immiscible fluids such as ethylbenzene 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 ethylbenzene fills the pores at the soil surface and begins to penetrate downward. The infiltration rate is governed by the saturated hydraulic conductivity (K_0) of ethylbenzene in the soil as described in the Introduction Manual. Surface ponding occurs when the spilling rate exceeds the infiltration rate. It is assumed that the ethylbenzene moves downward through the soil as a saturated slug, leaving behind a constant residual amount (S_0) of ethylbenzene within the soil pores.

Downward transport will continue until the volume of ethylbenzene spilled per unit area (B_0) equals the amount retained in the soil as S_0 . Some lateral spreading may occur due to capillary action. If B_0 is greater than the volume that can be retained as S_0 above the groundwater table, the excess ethylbenzene will spread as a pancake within the saturated groundwater capillary fringe. The resultant contaminated zone consists of a "vertical" column and "horizontal" pancakes of soil containing the residual amount of ethylbenzene, S_0 . This is shown schematically in Figure 24.

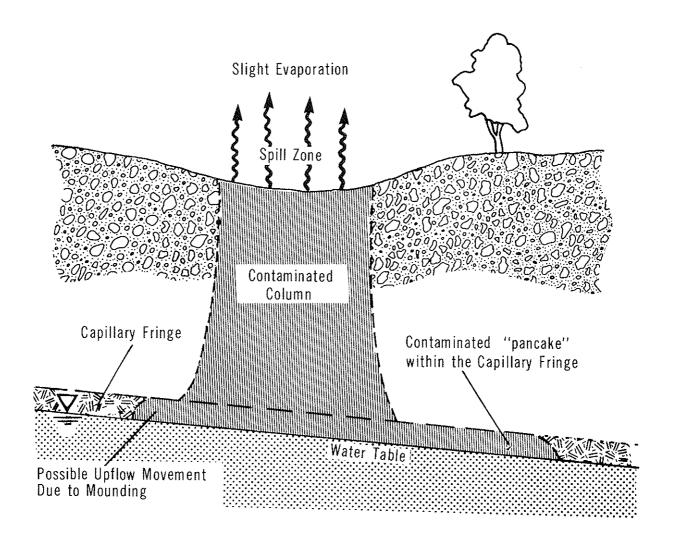
Since ethylbenzene is very slightly soluble in water, further contaminant migration can occur in the solution phase as precipitation continues to infiltrate through the contaminated zone. Adsorption onto soil, volatilization, and biodegradation can also be factors influencing the subsequent fate of ethylbenzene.

The rate of movement for the system described above is dependent on several factors involving properties of both the spill and the soil. The soil system can be particularly complex with respect to soil type and stratigraphy, and soil properties such as pH, moisture distribution, temperature and absorptive capacity at the time of the spill. While these properties can vary significantly from one location to another, such detailed analyses are assumed to be beyond the scope of this study and, as a result, more simplified techniques with broader applicability have been developed for this work. The resulting equations were used for nomogram development.

As described in the Introduction Manual, three soil types were considered in this study to reflect a broad range in hydraulic conductivity. The properties were taken to be uniform throughout the depth of penetration. Determination of S_0 , the fraction of the pore volume occupied by residual ethylbenzene, was based on the work of Blokker

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SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand -Porosity (n) = 0.35 -Intrinsic Permeability (k) = 10^{-9} m² -Field Capacity (θ_{fc}) = 0.075

(1971) on oil spills. Because of similar viscosities, the behaviour of ethylbenzene in soil was assumed to be similar to that of kerosene and light oil.

5.5.2 Penetration Nomograms. A flowchart for use of the nomograms is shown in Figure 25. The nomograms are presented in Figures 26, 27 and 28.

Note: The nomograms may be made to apply to spills of different magnitudes by multiplying both scales by the same factor.

T 2000	From Nomogram	Multiplier	New Values
T = 20°C Coarse Sand	B _o = 0.4 m ³ /m ² t _p = 41 min	0.1 0.1	B _o = 0.04 m ³ /m ² t _p = 4.1 min
	B = 23 m	0.1	B = 2.3 m

5.5.3 Sample Calculation. A 20 tonne spill of ethylbenzene 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 and check the corresponding evaporation loss.

Solution

Step 1: Define parameter	Step 1:	Define par	ameters
--------------------------	---------	------------	---------

- Mass spilled = 20,000 kg (20 tonnes)
- T = 20°C
- Mass density $\rho = 865 \text{ kg/m}^3$
- . r = 8.6 m

$$V = \frac{Mass}{\rho} = \frac{2 \times 10^{4} \text{ kg}}{865 \text{ kg/m}^{3}} = 23.1 \text{ m}^{3}$$
$$A = \pi r^{2} = 232 \text{ m}^{2}$$

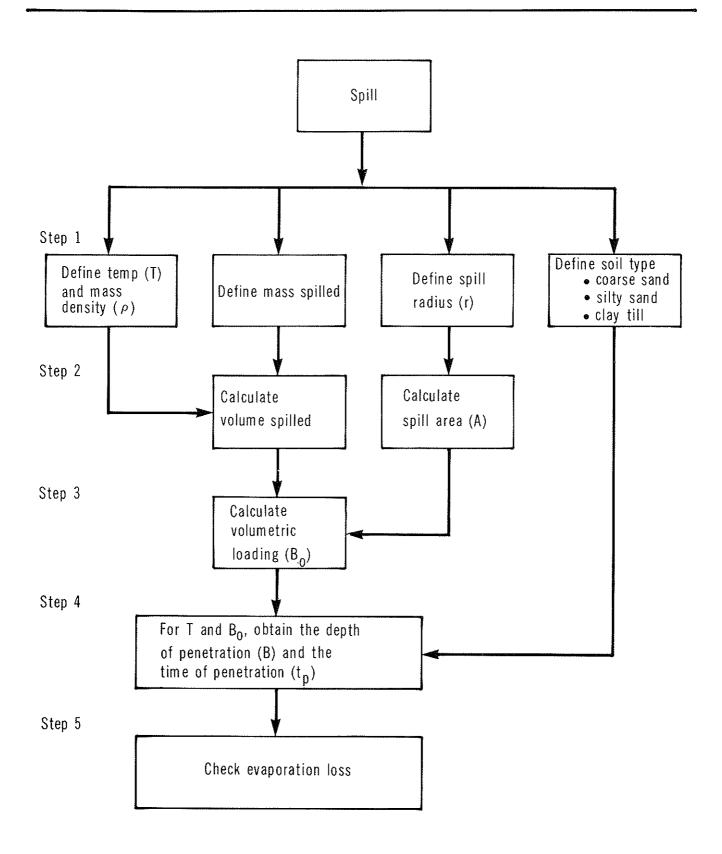
Step 3: Calculate volumetric loading B₀
. B₀ =
$$\frac{V}{A} = \frac{23.1 \text{ m}^3}{232 \text{ m}^2} = 0.1 \text{ m}^3/\text{m}^2$$

- Step 4: Estimate depth of penetration (B) and time of penetration (t_p)
 - For coarse sand, and with $B_0 = 0.1 \text{ m}^3/\text{m}^2$
 - B = 6 m, $t_D = 7 min$

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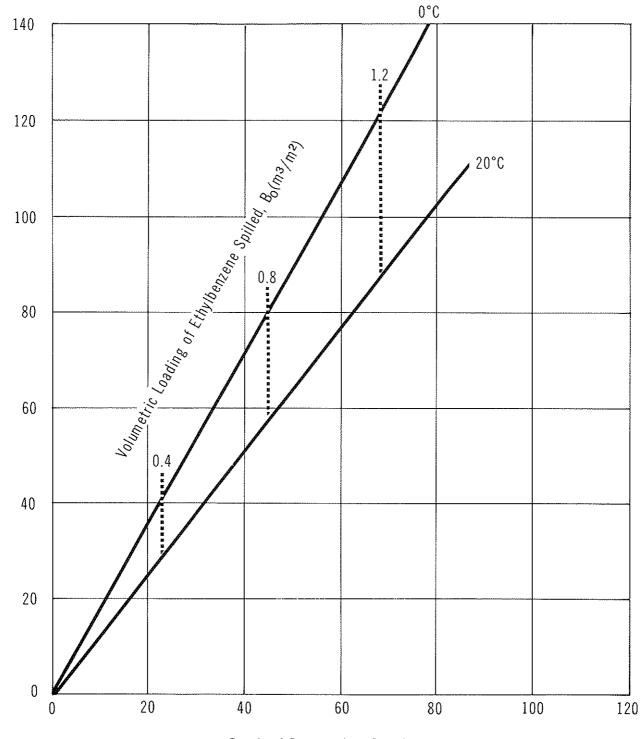
FLOWCHART FOR NOMOGRAM USE

FIGURE 25



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PENETRATION IN COARSE SAND



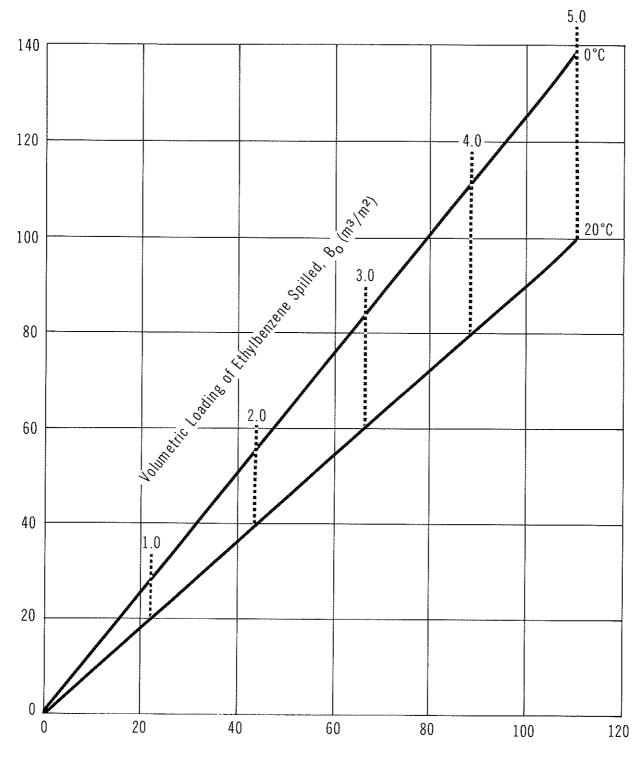
50

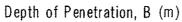
Depth of Penetration, B (m)

Time of Penetration, t_p (min)

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PENETRATION IN SILTY SAND



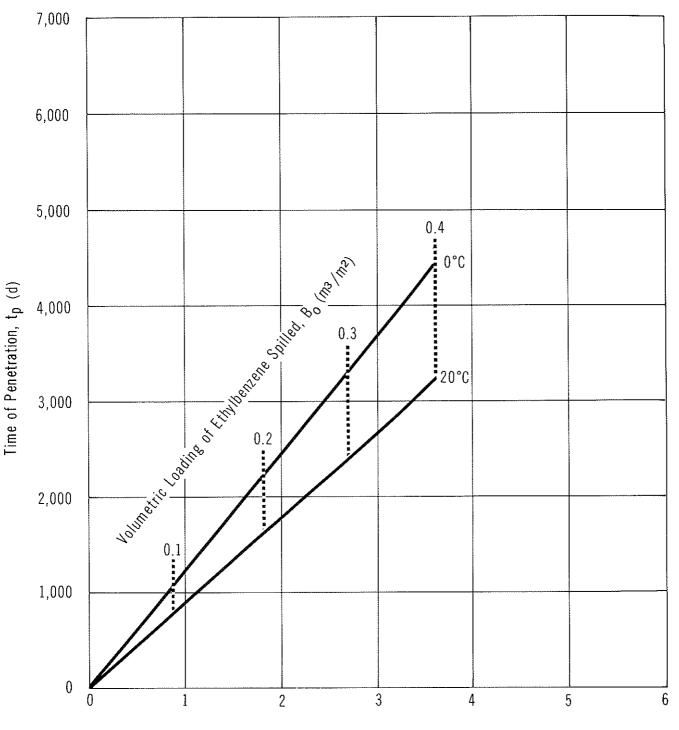


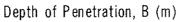
51

Time of Penetration, t_p (d)

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PENETRATION IN CLAY TILL





- Step 5: Check evaporation loss
 - . Use Figure 13, Section 5.3
 - With r = 8.6 m at 20°C, Q = 70 g/s or 7×10^{-2} kg/s
 - Evaporation Loss (E) = Q x t_p = 7 x 10⁻² kg/s x 7 min x 60 s/min = 29.4 kg

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Ethylbenzene levels in water are not currently regulated in Canada. In the United States, a limit of 0.25 mg/L has been recommended as a guideline to avoid tainting of fish and other organisms (WQC 1972). In the USSR, the maximum concentration permitted in reservoir water has been set at 0.1 mg/L, based on taste and odour effects (WQCDB-1 1970).

6.1.2 Air. The Ontario environmental air limit is 4,000 μ g/m³ (Ontario E.P. Act 1971). The ethylbenzene level in the ambient atmosphere (averaged over all stations in the U.S.) is approximately 44 μ g/m³ (PTP 1980).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Ethylbenzene has been assigned a TL_m 96 (4-day median lethal toxicity rating) of 100 to 10 ppm (= mg/L) (RTECS 1979).

6.2.2 Measured Toxicities.

		·····			~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	······
Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference	
Fish Tox	icity Tests					
0.44		Fathead minnow, embryo and larval stages	chronic effects occur		Fed. Reg.	1981
88	96	Bluegill	LC50	17°C	Johnson	1980
210	96	Channel catfish	LC50	22°C	Johnson	1980
14	96	Rainbow trout	LC50	12°C	Johnson	1980
4.3	96	Striped bass	LC50		ТМАЕ	1978
32	48 to 96	Bluegill	TLm	soft, 25°C	Middlebrook	s 1973
94	24 to 96	Goldfish	TLm	hard, 25°C	Middlebrook	s 1973
29	96	Bluegill	TLm		Pickering	1966
40	96	Bluntnose minnow	TLm		Pickering	1966
73	96	Goldfish	TLm		Pickering	1966
78	96	Guppy	TLm		Pickering	1966

6.2.2.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions Re	eference
<u>Fish Kill [</u>	Data				
50	24	Young coho salmon	100% mortality	artificial Ve seawater, 8°C	erschueren 1977
Invertebra	ites				
0.5	96	C. franciscorum	LC ₅₀	TM	MAE 1978
13	96	C. magister (crab larvae, stage 1)	LC ₅₀	ТМ	MAE 1978
Toxicity	· · · · · · · · · · · · · · · · · · ·	·····			
Threshold (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Microorga	<u>nisms</u>			98	······································
<u>></u> 100	not stated	Heterotrophic bacteria	adversely affected growth		EPA 560/ 11-80-018
12	16	Pseudomonas putida (bac- teria)	toxic; inhibited cell multi- plication	double-dis- tilled water, 25°C	Bringmann 1980
>160	7 days	Scenedesmus quadricauda (green algae)	toxic effect not stated	double-dis- tilled water, 27°C,	Bringmann 1980
140	72	Entosiphon sulcatum (protozoa)	toxic effec not stated	t double-dis- tilled water, 25°C	Bringmann 1980
33	not stated	Microcystis aeruginosa (algae)	toxic; inhibited cell multi- plication		Verschueren 1977
Conc. (mg/L)	Time (hours)	Species	Result	9 - Alfer als and an anna a star agus agus agus agus agus agus agus agus	Reference
Microfauna	<u> </u>				
75	48	Daphnia magna	EC ₅₀		AWQC 1980

6.2.2.2 Saltwater toxicity.

Conc. (mg/L)	Time (hours	s) Species		Result	Reference
Fish Toxi	city Tests				
0.43	96	Striped bass		LC ₅₀	AWQC 1980
275	96	Sheepshead m	ninnow	LC ₅₀	AWQC 1980
Microorg	<u>anisms</u>				
>438	96	Skeletonema costatum (dia	itom)	EC ₅₀ ; no adverse effects on cell number or chloro- phyll a production	AWQC 1980
Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Invertebr	ates				
87.6	96	Mysid shrimp	LC ₅₀		AWQC 1980
3.7	96	Bay shrimp	LC ₅₀		AWQC 1980
1,030	96	Pacific oyster	LC 50		AWQC 1980
10.2 to 17.3	24	Grass shrimp	no signi- ficant effect on larvae an adults, to LC50	ď	AWQC 1980
16	24	Nitrocra spinipes (copepod)	LC50	15 and 25 ppt salinity	AWQC 1980

6.2.3 Aquatic Studies. Acute toxicity of ethylbenzene to most freshwater aquatic life occurs at concentrations as low as 32 mg/L and would occur at lower concentrations among a few species that are more sensitive (AWQC 1980). Acute toxicity to most saltwater aquatic life occurs at concentrations as low as 0.43 mg/L and is lower among species more sensitive than those tested (AWQC 1980).

The chronic toxicity for freshwater and saltwater aquatic life has not yet been defined (AWQC 1980).

6.3 Other Air and Land Toxicity

Ethylbenzene is present in drinking waters and in the atmosphere. The sources include petroleum and petroleum by-products, motor vehicle exhaust, and cigarette smoke (AWQC 1980). Data from studies done in Switzerland, Germany, Japan and the U.S. indicate that ethylbenzene is significantly more abundant than styrene in the atmosphere (EPA 560/11-80-018).

6.4 Effect Studies

Ethylbenzene occurs in industrial effluents and the aquatic environment and may bind to sediment offering a potential for exposure to benthic organisms (Fed. Reg. 1981).

6.5 Degradation

6.5.1 B.O.D.

B.O.D. (% Theor.)	Conc. (ppm)	Time (days)	Seed	Method	Reference
<50	19 to 25 mg/L	35	Ohio River water	CO ₂ evolution	EPA 560/ 11-80-018
2.8		5	activated sludge	quiescent	Ryerman 1966
8.2		0.25	activated sludge	treatment- plant	Ryerman 1966
27	500	0.5	phenol-acclimated activated sludge		McKinney 1956

6.5.2 C.O.D. The C.O.D. (chemical oxygen demand) is 0.89 kg/kg (EPA 12020).

6.5.3 Biological Degradation. Several studies have attempted to determine the pathways of the microbial metabolism of ethylbenzene, using pure bacteria cultures. In general, oxidation can occur on the ring and on the side chain (EPA 560/11-80-018).

6.5.4 Chemical Degradation. Ethylbenzene is less reactive than styrene under smog conditions. It is not expected to hydrolyze in the environment (EPA 560/11-80-018).

6.5.5 Other Studies. Ethylbenzene is quite resistant to non-acclimated sludge cultures (OHM-TADS 1981). In a spill situation, no oxygen deficiencies are likely to develop (EPA 440/9-75-009).

The evaporation half-life of ethylbenzene from water (depth of 1 m) is 7.5 hours (EPA 560/11-80-018).

6.6 Long-term Fate and Effects

An ethylbenzene slick would pose an immediate hazard to waterfowl and marine animals (OHM-TADS 1981). Concentrations as low as 0.25 ppm can affect the taste of fish flesh and other aquatic organisms (Verschueren 1977). No data suggesting bioaccumulation or bioconcentration in aquatic organisms have been found (EPA 560/11-80-018).

7 HUMAN HEALTH

Although there is a considerable amount of information in the published literature concerning the toxicological effects of test animal inhalation exposures to ethylbenzene, controlled human studies detailing physiological effects are not encountered. Nor are incidents of ethylbenzene poisoning described in the literature. There is no information available to date on the effects of ethylbenzene exposure on reproduction, nor its mutagenicity or carcinogenicity.

Since 1976, only one research project on the toxicology of ethylbenzene has been reported in TOX TIPS (a summary of current research activity), and that project examined aquatic toxicity. Ethylbenzene has, however, been selected for carcinogenesis bioassay because of its large U.S. production volume (USDHEW - Carcinogen Report, 1980). Published work on ethylbenzene toxicology has been reviewed recently (EPA 560/11-80-018 and NRC 1981). The data summarized here are representative of information in the literature.

The toxicological data summarized here have been extracted from reliable standard reference sources only. 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 non-human mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

The exposure standards for ethylbenzene are based upon its irritant properties. Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Av	erages (TWA)		
TLV @ (8 h)	USA-ACGIH	100 ppm (435 mg/m ³)	TLV 1981
PEL (8 h)	USA-OSHA	100 ppm (435 mg/m ³)	GE 1978
Action Level	USA-OSHA	50 ppm (217 mg/m ³)	GE 1978
MIC (24 h)	USSR	0.005 ppm (0.02 mg/m ³)	Verschueren 1977
МАС	Poland	25 ppm	Doc. TLV 1980
МАС	Czech.	45 ppm	Doc. TLV 1980

Guideline (Time)	Origin	Recommended Level	Reference
Short-term Exposu	ire Limits (STEL)		
STEL (15 min)	USA-ACGIH	125 ppm (545 mg/m ³)	TLV 1981
Ceiling (15 min)	USA-OSHA	200 ppm (870 mg/m ³)	USDHEW 1977
Peak (5 min)	USA-OSHA	6,000 ppm (26,100 mg/m ³)	USDHEW 1977
MIC (30 min)	USSR	0.005 ppm (0.02 mg/m ³)	Verschueren 1977
<u>Other Human Toxi</u>	cities		
IDLH	USA-NIOSH	2,000 ppm (8,700 mg/m ³)	NIOSH Guide 1978
LCLO		No Data	
LDLO		No Data	
TC _{LO} (8 h)		100 ppm (435 mg/m ³)	RTECS (on-line) 1981

Inhalation Toxicity Index

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

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

At 20°C, ITI = 131.58

At -20°C, ITI = 10.53

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
10% in mineral oil (48 h patch test)	No irritation. No sensi- tization	Opdyke 1974. <u>IN</u> EPA 560/11-80-018
Neat	Absorption rates (n=7): 22 to 33 mg/cm ² /h, or 55 times that for benzene	Dutkiewicz 1967
112 to 156 mg/L (aq)	Absorption rates (n=14): 0.11 to 0.21 mg/cm ² /h. Estimated absorption via hands in saturated solution for 2 hours, or neat 1 hour, = 8 hours exposure to 25 ppm	Dutkiewicz 1967

Exposure Level		
(and Duration)	Effects	Reference
SPECIES: Rabbit		
5 g/kg	LD ₅₀	RTECS 1979
17.05* (14 d)	LD ₅₀	OHM-TADS 1981
17.8 mL/kg (single skin penetration)	LD50	Smyth 1962 . <u>IN</u> EPA <i>5</i> 60/11-80-018
15 mg (24 h)	Erythema	RTECS 1979
Skin swab (10 to 20 times)	Erythema, layer of devi- talized tissue	Wolf 1956. <u>IN</u> NRC 1981
Swab on uncovered belly	Moderate irritation	Smyth 1962. <u>IN</u> EPA 560/11-80-018
Swab on intact or abraded skin (24 h occlusion)	Moderate irritation	Opdyke 1975

* Units unstated

7.2.2 Eye Contact.

Exposure Level		
(and Duration)	Effects	Reference
SPECIES: Human		
5,000 ppm	Intolerable irritation of eyes and nose	Yant 1930. <u>IN</u> Proctor 1978
2,000 ppm	Lacrimation, nasal irritation	Yant 1930. <u>IN</u> Proctor 1978
1,000 ppm	Eye irritation. Tolerance developed	Yant 1930. <u>IN</u> Proctor 1978
200 ppm	TD _{LO}	OHM-TADS 1981
SPECIES: Guinea Pig		
1,000 ppm	Eye irritation	Yant 1930. <u>IN</u> Proctor 1978
SPECIES: Rabbit		
100 mg (single application)	Slight conjunctival irritation, no corneal injury	RTECS 1979

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7.3 Threshold Perception Properties

7.3.1 Odour.

Parameter	Media	Concentration	Reference
Odour Threshold	In water In water	140 ppm 0.2 mg/L	ASTM 1980 ASTM 1980
Lower Threshold	In air	0.25 ppm	OHM-TADS 1981

7.3.2 Taste.

Parameter	Media	Concentration	Reference
Taste Threshold	In water	0.1 mg/L	ASTM 1980
	not specified	0.25 ppm	OHM-TADS 1981

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level		
(and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
1,000 to 5,000 ppm	Lacrimation, dizziness, central nervous system effects	Patty 1981
100 ppm (8 h)	TC _{LO} . Irritation	RTECS 1979
85 ppm	Irritation, fatigue, headache	Patty 1981
23 to 85 ppm (8 h)	Excreted as urinary mandelic acid (64%). Suggested parameter for biological TLV	Bardodej 1970
Occupational exposure - styrene workers	After 3 days unexposed, ethylben- zene detectable in subcutaneous fat. Persistence greater than that of styrene	Wolf 1956. <u>IN</u> NRC 1981

Exposure Level		· · · · · · · · · · · · · · · · · · ·
(and Duration)	Effects	Reference
SPECIES: Unspecified		
10,000 ppm (18 min)	Vertigo, unsteadiness, ataxia, unconsciousness	Browning. <u>IN</u> TDB (on-line) 1981
2,000 ppm (375 min)	Motor ataxia, unconsciousness	Browning. <u>IN</u> TDB (on-line) 1981
SPECIES: Guinea Pig		
10,000 ppm	LCLO	RTECS 1979
10,000 ppm	Death in 2 to 3 hours	Yant 1930. <u>IN</u> Proctor 1978
5,000 ppm	Death in 8 hours	Yant 1930 . <u>IN</u> Proctor 1978
SPECIES: Rabbit		
99 ppm	TC_{LO} (1 to 18 d preg.)	RTECS (on-line) 1981
SPECIES: Rat		
16,122 to 17,273 ppm (2 h)	LC100	Ivanov 1962. <u>IN</u> EPA 560/11-80-018
13,367 ppm (2 h)	LC ₅₀	Ivanov 1962 . <u>IN</u> EPA 560/11-80-018
4,000 ppm (4 h)	LC ₅₀	Smyth 1962. <u>IN</u> EPA 560/11-80-018
4,000 ppm	LCLO	RTECS 1979
985 ppm (7 h)	TC _{LO} (1 to 19 d preg.)	RTECS (on-line) 1981
97 ppm (7 h)	TC _{LO} (15 d preg.)	RTECS (on-line) 1981
96 ppm (7 h)	TC_{LO} (1 to 19 d preg.)	RTECS (on-line) 1981
SPECIES: Mouse		
11,500 ppm	Death	Patty. <u>IN</u> TDB (on-line) 1981
2,300 to 3,500 ppm	Minimum concentration to cause prostration	Patty. <u>IN</u> TDB (on-line) 1981

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Exposure Level (and Duration)	Effects	Reference
Chronic Exposures		
SPECIES: Rhesus Monkey		
600 ppm (130 x 7 h exposures in 186 d)	Slight testes histopathology, increase in liver weight	Wolf 1956. <u>IN</u> NRC 1981
400 ppm (130 x 7 h exposures in 186 d)	No effect	Wolf 1956. <u>IN</u> NRC 1981
SPECIES: Guinea Pig		
1,250 ppm (138 x 7 h exposures in 214 d)	Slight growth depression	Wolf 1956. <u>IN</u> NRC 1981
600 ppm (130 x 7 h exposures in 186 d)	Slight increase in liver weight	Wolf 1956. <u>IN</u> NRC 1981
400 ppm (130 x 7 h exposures in 186 d)	No effect	Wolf 1956. <u>IN</u> NRC 1981
SPECIES: Rabbit		
1,250 ppm (138 x 7 h exposures in 214 d)	Not stated	Wolf 1956. <u>IN</u> NRC 1981
600 ppm (130 x 7 h exposures in 186 d)	Slight testes histopathology	Wolf 1956. <u>IN</u> NRC 1981
400 ppm (130 x 7 h exposures in 186 d)	No effect	Wolf 1956. <u>IN</u> NRC 1981
230 ppm (4 h per day for 7 months)	Muscle chronaria changes, disturbed blood cholinesterase activity, decreased plasma albumin, increased plasma globulins, leukocytosis, dystrophic changes in liver, kidneys. (i.e., may affect hematopoiesis but chemical significance not yet determined)	Ivanov 1964. <u>IN</u> EPA 560/11-80-018
SPECIES: Rat		
2,200 ppm (103 x 7 h exposures in 144 d)	Moderate kidney weight increase, growth depression	Wolf 1956. <u>IN</u> NRC 1981
1,250 ppm (138 x 7 h exposures in 214 d)	Slight kidney and liver weight increase and histopathology, slight growth depression	Wolf 1956. <u>IN</u> NRC 1981

Exposure Level (and Duration)	Effects	Reference
600 ppm (130 x 7 h exposures in 180 d)	Slight kidney and liver weight increase	Wolf 1956. <u>IN</u> NRC 1981
400 ppm (130 x 7 h exposures in 186 d)	Slight kidney and liver weight increase	Wolf 1956. <u>IN</u> NRC 1981
Saturated vapour (1 h)	LC	OHM-TADS 1981

7.4.2 Ingestion.

1.00

Exposure Level (and Duration)		Defense
	E.ffects	Reference
Acute Exposure		
SPECIES: Human		
5 g/kg	LD ₅₀	Dreisbach 1980
SPECIES: Rat		
6 g/kg	LD ₁₀₀	Faustav 1960. IN EPA 560/11-80-018
4 . 94 g/kg	LD ₅₀	Smyth 1962 . <u>IN</u> EPA 560/11-80-018
5.64 mL/kg	LD ₅₀	EPA 560/11-80-018
3.5 g/kg	LD ₅₀ (n=57)	Wolf 1956. <u>IN</u> NRC 1981
0.25 mL	Aspiration into lungs. CNS stimulation, cardiac arrest, respiratory paralysis, death	Gerarde 1963. <u>IN</u> EPA 560/11-80-018
Chronic Exposures		
SPECIES: Rat		
680 mg/kg/d (130 of 182 d)	Slight increase in liver and kidney weights, slight histopathological effects	Wolf 1956. <u>IN</u> EPA 560/11-80-018

Exposure Level (and Duration)	Effects	Reference
408 mg/kg/d (130 of 182 d)	Slight increase in liver and kidney weights, slight histopathological effects	Wolf 1956. <u>IN</u> EPA 560/11-80-018
136 mg/kg/d (130 of 182 d)	No effect	Wolf 1956. <u>IN</u> EPA 560/11-80-018
5,231* (14 d)	LD50	OHM-TADS 1981

* Units unstated

7.4.3 Subcutaneous.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human 1,000 ppm	TC _{LO}	OHM-TADS 1981
SPECIES: Rabbit 5,000 mg/kg	LD50	OHM-TADS 1981

7.5 Symptoms of Exposure

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

7.5.1 Inhalation.

- 1. Irritation of mucous membranes nose, eyes, throat.
- 2. Lacrimation.
- 3. Constriction of the chest (ITII 1981; Sax 1979).
- 4. Dizziness, vertigo, ataxia (Doc. TLV 1980; Proctor 1978).
- 5. Headache (GE 1978).
- 6. Inflammation of the upper respiratory tract mucosa (Ency. OHS 1971. IN TDB (online) 1981).
- 7. Depression of the central nervous system, narcosis.

- 8. Cramps (USDHEW 1977).
- 9. Toxic hepatitis (Ency. OHS 1971. IN TDB (on-line) 1981).
- Hematological disorders leukopenia and lymphocytosis (Ency. OHS 1971. <u>IN</u> TDB (on-line) 1981).
- 11. Coma.
- 12. Death due to respiratory centre paralysis (Sax 1979; USDHEW 1977).
- Pathological findings congestion of brain and lungs with edema (Sax 1979), foci of epithelial necrosis in renal tubules and hepatic dystrophy (Ency. OHS 1971. <u>IN</u> TDB (on-line) 1981).

7.5.2 Ingestion.

- 1. Irritation of the gastrointestinal tract (Dreisbach 1980).
- 2. Manifestations in the central nervous system (Dreisbach 1980).

7.5.3 Skin Contact.

- 1. Irritation. Defatting of the skin.
- 2. Erythema and inflammation (Sax 1979).
- 3. Repeated or prolonged contact results in dry and scaly dermatitis.

7.5.4 Eye Contact.

- 1. Irritation.
- 2. Conjunctival irritation (Haley 1981; Proctor 1978).

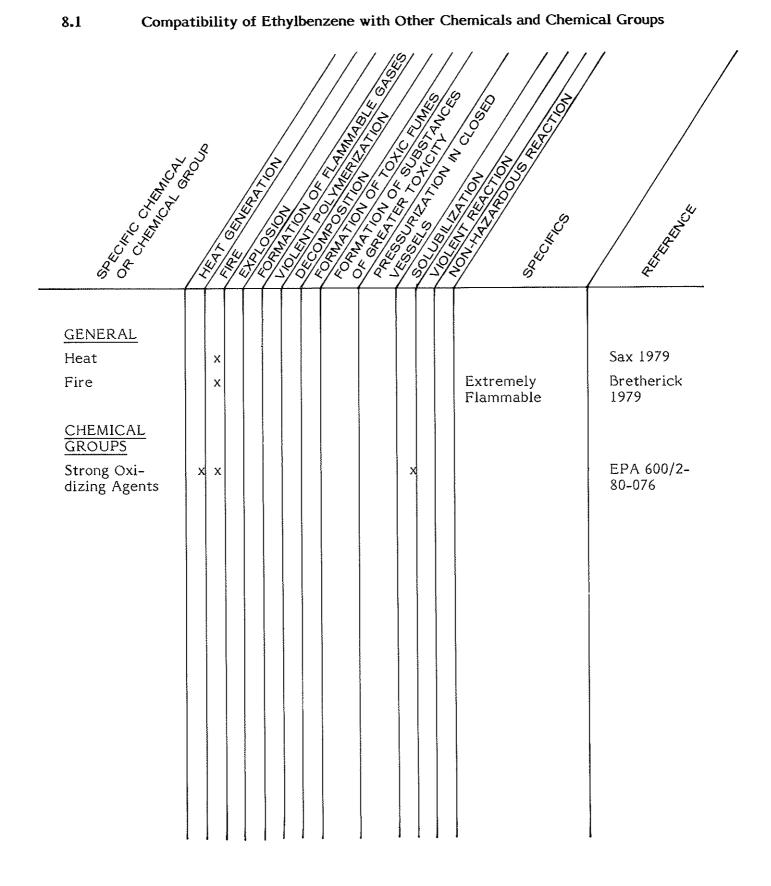
7.6 Human Toxicity to Decay or Combustion Products

The combustion products of ethylbenzene are water and carbon dioxide (see Section 2.3) or carbon monoxide in limited oxygen atmospheres.

7.6.1 Carbon Monoxide and Carbon Dioxide. Carbon monoxide is a colourless, practically odourless gas which is a chemical asphyxiant. It causes hypoxia by complexing with hemoglobin and reducing the oxygen-carrying capacity of the blood. Excessive exposure will result in death from asphyxiation. More moderate exposure may cause headaches and affect mental functions. The effects of moderate exposures are reversible, although considerable time is required to reverse the carbon-monoxide-hemoglobin complexing reaction. The TLV® for carbon monoxide is 50 ppm (8 h - TWA) and 400 ppm (STEL) (Doc. TLV 1980).

Carbon dioxide is a colourless, odourless gas which in elevated concentrations may act to produce mild narcotic effects, respiratory stimulation, and asphyxiation. Its TLV® is 5,000 ppm (8 h - TWA) and 15,000 ppm (STEL) (Doc. TLV 1980).

8 CHEMICAL COMPATIBILITY



9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged – in so doing, it is recognized that there may be some discrepancies between different sources of information. These procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Flammable liquid can readily form explosive mixtures with air especially when heated. Vapours may flow along surfaces to reach distant ignition sources, and flashback. Burning of the contents can produce toxic products, such as carbon monoxide (GE 1978).

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to help prevent rupture. Water may be ineffective for putting out fire (NFPA 1978; GE 1978).

- Small fires: Dry chemical, CO₂, water spray or alcohol foam. Sand or earth may also be used (CCPA 1982).
- Large fires: Water spray, fog or alcohol foam. AFFF and ATC foams (CCPA 1982).

Move containers from fire area if this can be done without risk. Stay away from ends of tanks. For massive fire in cargo area, use unmanned hose holder or monitor nozzles (ERG 1980). Spilled liquid should be covered with a layer of foam (AFFF or ATC types are recommended) (CCPA 1982). If foam is not available, a light fog pattern may be applied. Do not use a straight stream as this will spread the spill (CCPA 1982).

9.1.3 Spill Actions.

9.1.3.1 General. Stop discharge of material if this can be done without risk. Eliminate all sources of ignition and smoking. Use non-sparking tools when working with this material. Containers must be electrically bonded and grounded before transferring the liquid. Safety cans may be used for small amounts. Avoid skin contact and inhalation (GE 1978).

Use water spray to reduce vapours (ERG 1980). Application of fluorocarbon water foam to diminish vapours should also be considered (EPA 670/2-75-042).

9.1.3.2 Spills on land. Contain if possible and remove free liquid with explosion-proof equipment. Soak up residue with sand, earth or vermiculite and shovel into metal containers with covers for disposal (ERG 1980; GE 1978). If containment is not possible, direct spilled material to a holding area for future handling (GE 1978). Application of fly ash or cement powder to absorb the liquid bulk should be considered. Application of universal gelling agent may also be used to immobilize the spill (EPA 670/2-75-042).

9.1.3.3 Spills on water. Contain if possible with booms or natural barriers to limit spreading. Use surface-acting agents to compress and thicken spilled material. Remove trapped material with suction hoses (EPA 670/2-75-042).

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills on land. After the spilled material has been collected into a holding area, (oil) skimming equipment and/or sorbent (polyurethane) foams can be used to remove the slick (OHM-TADS 1981). Use of activated carbon on dissolved portion is recommended (EPA 670/2-75-042). Combustible sorbents should not be used (CCPA 1982).

9.1.4.2 Spills on water. After containment, (oil) skimming equipment and/or sorbent (polyurethane) foams can be used to remove the slick (OHM-TADS 1981). Injection of universal gelling agent to solidify trapped mass should also be considered. Activated carbon can be applied to the dissolved portion. Use mechanical dredges or lifts to remove immobilized masses of pollutants for disposal (EPA 670/2-75-042).

9.1.4.3 General. For treatment of contaminated water, gravity separation of the solids followed by skimming of surface to remove spilled material is recommended. If skimming is not sufficient, dual media filtration followed by carbon adsorption is also recommended. Recommended carbon ratio is 1.0 kg to 10.0 kg soluble material (EPA 600/2-77-227).

The following treatment processes have shown possible applicability for spill countermeasures:

Process	% Removal (TSA 1980)	Process	Maximum % Removal (EPA 600/8-80-042E)
Biological	90 to 100	Clarification/Sedimentation	64
Coagulation/ Precipitation	56	Clarification/Sedimentation with Chemical Addition (Alum, Polymer)	> 94

Process	% Removal (TSA 1980)	Process	R	aximum % emoval (EPA 00/8-80-042E)
Stripping	80 to 93	Clarification/Sedimentation with Chemical Addition (Polymer)		81
Solvent Extraction	97	Clarification /Sedimentation with Chemical Addition (Alum, Lime)	>	96
Carbon Adsorption	50 to 84	Gas Flotation (Dissolved Air Flotation)		99
		Gas Flotation with Chemical Addition (Calcium Chloride Polymer)	>	99
		Gas Flotation with Chemical Addition (Polymer)		65
		Granular Media Filtration	>	99
		Activated Sludge	>	99
		Lagoon (Aerated)	>	94
		Solvent Extraction		97
		Powdered Carbon Addition (with Activated Sludge)		84

9.1.5 Charcoal Filtration Data (EPA 600/8-80-023). The following values recommended for the removal of ethylbenzene in water by either the single stage powdered carbon contactor or the granular carbon column adsorption system were obtained using the Freundlich Adsorption equation. The derivation of the equation is discussed in the Introduction Manual. The values of Freundlich parameters used are k=53; 1/n=0.79.

SINGLE STAGE POWDERED CARBON CONTACTOR SYSTEM					
Initial Concentration (mg/L)	Carbon Doses (mg/L)	Final Concentration (mg/L)			
1.0	110	0.1			
1.0	710	0.01			
1.0	4,400	0.001			
0.1	65	0.1			
0.1	440	0.001			
0.01	40	0.001			

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GRANULAR CARBON COLUMN SYSTEM (ESTIMATED)				
Initial Concentration (mg/L)	Breakthrough Carbon Doses (mg/L)			
1.0	19			
0.1	12			
0.01	7.2			

These carbon doses were reported for water with neutral pH.

9.1.6 Disposal. Waste ethylbenzene must never be discharged directly into sewers or surface waters. The material can be burned in approved incinerators (GE 1978). Additional flammable solvent may be added to assist burning of the material (OHM-TADS 1981). Following treatment, either at the spill site or at a waste management facility, the resultant sludge can be disposed in a secure landfill.

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

If the spilled material is known to be ethylbenzene:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent any possibility of repeated or prolonged skin contact with liquid ethylbenzene (NIOSH/OSHA 1981).
- Any clothing which becomes wet with liquid ethylbenzene should be removed immediately and not reworn until the ethylbenzene is removed from the clothing (NIOSH/OSHA 1981).
- Personnel should be provided with and required to use splash-proof safety goggles where liquid ethylbenzene may contact the eyes (NIOSH/OSHA 1981). Chemical safety goggles are also recommended where splashing in the eyes may occur (GE 1978).

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

Condition	Minimum Respiratory Protection* Required Above 100 ppm			
Vapour Concentration 1,000 ppm or less	A chemical cartridge respirator with a full face- piece and an organic vapour cartridge(s).			
2,000 ppm or less	A gas mask with a chin-style or a front- or back- mounted organic vapour canister.			
	Any supplied-air respirator with a full facepiece, helmet, or hood.			
	Any self-contained breathing apparatus with a full facepiece.			
Greater than 2,000 ppm, or entry to and escape from unknown concentrations	Self-contained breathing apparatus with a full face- piece operated in pressure-demand or other positive pressure mode.			
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.			
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.			
Escape	Any gas mask providing protection against organic vapours.			
	Any escape self-contained breathing apparatus.			

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

9.1.8 Special Precautions. Store this material in tightly closed containers in cool, well-ventilated areas, away from oxidizing agents, strong acids and bases, ammonia, heat and sources of ignition (GE 1978).

9.2 Specialized Countermeasures Equipment, Materials or Systems

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

Recovery from Water: Universal Gelling Agent

Treating Agents: Hazorb (sorbent)

10 PREVIOUS SPILL EXPERIENCE

This Section contains information on previous spill experience which will be useful to readers planning spill response. Only those which meet these 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 revision to include the most information.

10.1 Plant Spill (Personal Communication with EPS and MOE)

During transfer of ethylbenzene in a petrochemical plant, the stream and drain valve were left open while unattended which resulted in a spill of approximately 240,000 litres of material in a storm sewer. Evacuation of plant personnel was initiated and a dyking arrangement was constructed at the storm sewer outlet. Due to the increase in vapour explosion hazard in the sewer system, the dyke was removed and approximately 190,000 litres of material flowed into a major watercourse.

Vapour traps using water were formed along the sewer line at locations potentially dangerous. Explosion-proof air blowers were also used to direct vapours away from danger areas. Approximately 48,000 litres of spilled material were recovered by vacuum trucks and disposed of at a nearby incinerator.

A fish kill was noted in the watercourse. A continuous water monitoring station, approximately 600 m downstream of the spill, indicated that ethylbenzene had reached this area.

The authors feel that this incident shows the need for better containment methodology for the area between the sewer outfall and the watercourse, and also illustrates the need for contingency planning for these events.

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ANALYTICAL METHODS

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

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

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

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

11.1 Quantitative Method for the Detection of Ethylbenzene in Air

Gas Chromatography (NIOSH 1977). A range of 222 to 884 mg/m^3 (50 to 200 11.1.1 ppm) ethylbenzene in air may be analyzed by gas chromatography (GC). This is currently the most practical method for identifying and measuring many volatile organic compounds. Retention time or Kovats index is used to identify the compound but positive identification requires the use of more than one column, special detectors, spiking the sample with the suspected component or combining GC with mass spectroscopy (MS).

A known volume of air is drawn through a glass sampling tube. The front section is packed with 100 mg of activated charcoal which is separated from 50 mg of charcoal in the back section by a 2 mm section of urethane foam. A 10 L air sample is recommended but this should be reduced if there is a large amount of ethylbenzene present. Maximum tube loading should be 16 mg. The sample is desorbed with 0.5 mL carbon disulphide. Desorption efficiency is 100 percent. Analysis is by GC with a flame ionization detector (FID), using a column packed with 10 percent FFAP on 80/100 mesh acid-washed DMCS chromosorb W. In high humidity, the condensation of water vapour

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reduces the collection efficiency of the charcoal and the concentration of ethylbenzene may appear to be lower than it actually is. The loss of sample through overloading the charcoal tube may also produce lower results. An advantage of this method is that in the event of a mixed spill two or more substances may be analyzed simultaneously.

Other sample collection methods may be useful in certain circumstances. The air sample may be collected in a glass vessel for on-site analysis or for transportation to a laboratory (Jones 1976; IERL 1976). Where a GC is used at a spill site, an automated gas sampling valve may be used. Outside air is injected directly through a 1 cm³ sampling loop by means of a diaphragm pump (Hester 1979). This is useful for ongoing monitoring.

Alternate columns are 10 percent Carbowax on 80/100 mesh chromosorb W (ASTM 1981), 10 percent 1,2,3-tris(2-cyanoethoxy)propane on 100/200 mesh chromosorb PAW (Hester 1979), and 1 percent OV-101 (or SE-30) on 100/120 mesh chromosorb W (Jones 1976; IERL 1976).

The use of a photoionization detector (PID), rather than a flame ionization detector (FID), allows analysis at the sub-ppm level without pre-concentration or trapping. Sample dilution may be necessary if GC-PID is used as a vehicle-portable method and transported to the spill site where the concentration may exceed the range of the detector (Hester 1979).

11.2 Qualitative Method for the Detection of Ethylbenzene in Air

Air is drawn through a glass tube as in Section 11.1.1. The sample is desorbed with chloroform and identified using the Friedel-Crafts alkylation reaction. About 100 mg of anhydrous aluminum chloride is placed in a test tube and heated until it sublimes. When it has cooled, a drop of the extract and two drops of chloroform are added with shaking. The appearance of an orange-red colour indicates the presence of an aromatic ring (Owen 1969).

11.3 Quantitative Methods for the Detection of Ethylbenzene in Water

11.3.1 Gas Chromatography (ASTM 1979). Concentrations of ethylbenzene greater than 1 ppm can be measured by direct injection of the water sample into the gas chromatograph (GC). This is the method of choice when the identification of a spill is necessary or when low levels of ethylbenzene are present (see Section 11.1.1).

A representative sample is collected in a glass bottle. Analysis is by GC using various columns and detectors as described in Section 11.1.1. If the sample concentration is less than 1 ppm, the sample may be concentrated by evaporation, freeze-out, solvent

extraction or adsorption on activated charcoal. Highly concentrated samples may be diluted. Particulate or suspended matter must be removed by centrifugation or membrane filtration. Acidification of the sample will help to dissolve particulate matter. An advantage of the GC method is that in the event of a mixed spill, two or more substances may be separated and analyzed. This method can be combined with mass spectroscopy for positive identification of the sample.

11.3.2 Infrared Spectroscopy (AWWA 1976). Concentrations of 4 to 40 ppm ethylbenzene in water can be measured using 1 cm path length cells with a precision of \pm 10 percent.

Approximately 1 litre of water is collected, the volume determined accurately and the sample acidified with hydrochloric acid. The ethylbenzene is extracted using Freon 113° (1,1,2-trichloro-1,2,2-trifluoroethane). Recovery is 99 percent. Using matched quartz cells with Freon° in the reference beam of a double-beam IR recording spectrophotometer, the sample is scanned from 3,200 cm⁻¹ to 2,700 cm⁻¹. The advantage of this method over methods that involve heating the sample is that sample loss through volatilization is minimized. This method lacks high sensitivity but is adequate for spills. It is not specific and assumes that the identity of the spill is known.

11.3.3 Gravimetric (AWWA 1976). This method is suitable for concentrations of ethylbenzene greater than 10 ppm. The precision is \pm 6 percent.

Approximately 1 litre of sample is collected, the volume determined accurately and the sample acidified with hydrochloric acid. The ethylbenzene is extracted using Freon 113[®] (1,1,2-trichloro-1,2,2-trifluoroethane). Recovery is 99 percent. The Freon[®] is distilled from the extraction flask on a water bath at 70°C. Sample loss may be a problem if the temperature is not carefully controlled. Air is drawn through the flask for the final 1 minute to remove all traces of the Freon[®]. The flask is cooled and weighed. This is a simple and inexpensive method which does not require complex instrumentation. It is not highly sensitive or specific but is adequate for spills of a known composition.

11.4 Qualitative Method for the Detection of Ethylbenzene in Water

The water sample is extracted with chloroform and the Friedel-Crafts alkylation reaction is used to identify aromatic hydrocarbons. About 100 mg of anhydrous aluminum chloride is placed in a test tube and heated until it sublimes. When it has cooled, a drop of the extract and two drops of chloroform are added with shaking. The appearance of an orange-red colour indicates the presence of an aromatic ring (Owen 1969).

The infrared spectroscopy method discussed in Section 11.3.2 may be used for qualitative identification by observing the presence of absorption bands between $3,200 \text{ cm}^{-1}$ and $2,700 \text{ cm}^{-1}$ (AWWA 1976).

11.5 Quantitative Methods for the Detection of Ethylbenzene in Soil

11.5.1 Gas Chromatography (NIOSH 1977; ASTM 1979). Concentrations of ethylbenzene at the ppm level may be detected using a flame ionization detector. The detection limit may be extended to the ppb level by the use of a photoionization detector.

Approximately 20 g of soil, accurately weighed, is collected in a glass jar and dried by the addition of magnesium sulphate. Freon 113° (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract ethylbenzene from the soil. The Freon° is distilled from the extraction flask on a water bath at 70°C. Sample loss may be a problem if the temperature is not carefully controlled. Air is drawn through the flask for the final 1 minute to remove all traces of the Freon°. The residue is dissolved in carbon disulphide. This is injected into a gas chromatograph equipped with a column and detector as described in Section 11.1.1. This is the method of choice when the identification of a spill is necessary or when low levels of ethylbenzene are present.

11.5.2 Infrared Spectroscopy (AWWA 1976). Concentrations of 4 to 40 ppm ethylbenzene in soil may be measured using 1 cm path length cells.

Approximately 20 g of soil, accurately weighed, is collected in a glass jar and dried by the addition of magnesium sulphate. Freon 113° (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the ethylbenzene from the soil. Using quartz cells with Freon° in the reference beam of a double-beam IR recording spectrophotometer, the sample is scanned from 3,200 cm⁻¹ to 2,700 cm⁻¹. This is a simple, inexpensive method. It lacks sensitivity but is adequate for spills of a known composition.

11.5.3 Gravimetric (AWWA 1976). This method is used for the detection of concentrations greater than 10 ppm ethylbenzene in soil.

Approximately 20 g of soil, accurately weighed, is collected in a glass jar and dried by the addition of magnesium sulphate. Freon 113[®] (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the ethylbenzene then distilled from the extraction flask on a water bath. A temperature of 70°C must be carefully controlled or sample loss will be a problem. Air is drawn through the flask for the final 1 minute. The flask is

cooled and weighed. This is a simple, inexpensive method. It lacks sensitivity and specificity, but is adequate for spills of a known composition.

11.6 Qualitative Method for the Detection of Ethylbenzene in Soil

The Friedel-Crafts alkylation reaction is used to identify aromatic hydrocarbons. A sample of soil is extracted with Freon 113° (1,1,2-trichloro-1,2,2trifluoroethane), and the Freon° evaporated as in Section 11.5.3 above. The residue is taken up in chloroform. Approximately 100 mg of anhydrous aluminum chloride is placed in a test tube and heated until it sublimes.

When it has cooled, several drops of the chloroform containing the residue are added with shaking. The appearance of an orange-red colour indicates the presence of a compound containing an aromatic ring (Owen 1969).

The infrared spectroscopy method discussed in Section 11.5.2 may be used for qualitative identification of ethylbenzene by observing the presence of absorption bands between $3,200 \text{ cm}^{-1}$ and $2,700 \text{ cm}^{-1}$ (AWWA 1976).

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand	MMAD	mass median aerodynamic
b.p.	boiling point		diameter
CC	closed cup	MMD	mass median diameter
cm	centimetre	m.p.	melting point
CMD	count median diameter	MW	molecular weight
COD	chemical oxygen demand	N	newton
conc.	concentration	NAS	National Academy of Sciences
c.t.	critical temperature	NFPA	National Fire Protection
eV	electron volt		Association
g	gram	NIOSH	National Institute for
ha	hectare		Occupational Safety and
Hg	mercury		Health
IDLH	immediately dangerous to		
	life and health	nm	nanometre
Imp. gal.	imperial gallon	0	ortho
in.	inch	OC	open cup
J	joule	p	para
kg	kilogram	PC	critical pressure
kĴ	kilojoule	PEL	permissible exposure level
km	kilometre	pН	measure of acidity/
kPa	kilopascal	L. C. C.	alkalinity
kt	kilotonne	ppb	parts per billion
L	litre	ppm	parts per million
lb.	pound	Ps	standard pressure
LC 50	lethal concentration fifty	psi	pounds per square inch
LCLO	lethal concentration low	S	second
LD 50	lethal dose fifty	STEL	short-term exposure limit
LDLO	lethal dose low	STIL	short-term inhalation limit
LEL	lower explosive limit	T _c	critical temperature
LFL	lower flammability limit	TCLO	toxic concentration low
m	metre	Td	decomposition temperature
m	meta	TDLO	toxic dose low
М	molar	TLm	median tolerance limit
MAC	maximum acceptable con-	TLV	Threshold Limit Value
	centration	T _s	standard temperature
max	maximum	TWA	time weighted average
mg	milligram	UEL	upper explosive limit
MIC	maximum immision	UFL	upper flammability limit
	concentration	VMD	volume mean diameter
min	minute or minimum	v/v	volume per volume
mm	millimetre	w/w	weight per weight
- 1997 (1977) (1977)		al m	"ergin per wergin
μg	microgram		

μm °Be

micrometre degrees Baumé (density)