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## INTRODUCTION MANUAL

August 1985

Canada

## **ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS**

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

## **INTRODUCTION MANUAL**

## **ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS**

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

August 1985

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## FOREWORD

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

## ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation and Waterloo Engineering Limited.



# TABLE OF CONTENTS

	Page
FOREWORD	i
ACKNOWLEDGEMENTS	i
LIST OF FIGURES	vi
LIST OF TABLES	vii
INTRODUCTION	1
1 SUMMARY	4
1.1 Overview and Objectives	4
1.2 Selection and Presentation of Data	4
2 PHYSICAL AND CHEMICAL DATA	5
2.1 Overview and Objectives	5
2.2 Information Sources	5
2.3 Special Cases	5
2.3.1 Fire Properties	5
2.3.2 Solubility	5
2.4 Glossary of Chemical and Physical Terms	6
2.5 Derivation of Phase Diagrams	13
2.5.1 General Introduction	13
2.5.2 Methods for Estimating Phase Diagrams	14
2.5.2.1 Estimation of the liquid-vapour equilibrium	14
2.5.2.2 Estimation of the solid-vapour equilibrium	17
2.5.2.3 Estimation of the solid-liquid equilibrium	18
3 COMMERCE AND PRODUCTION	23
4 MATERIAL HANDLING AND COMPATIBILITY	24
4.1 Overview and Objectives	24
4.2 Information Sources	24
4.3 Selection and Presentation of Data	25
5 CONTAMINANT TRANSPORT	26
5.1 Introduction	26
5.2 Leak Nomograms	26
5.2.1 Overview and Objectives	26
5.2.2 Information Sources	26
5.2.3 Selection of Conditions and Calculation of Data	27
5.2.3.1 Size and location of puncture	27
5.2.3.2 Liquid venting	27
5.2.3.3 Gas venting or release	28

	Page
5.2.3.4	29
5.3	30
5.3.1	30
5.3.2	31
5.3.3	33
5.3.3.1	35
5.3.3.2	35
5.3.3.3	36
5.3.3.4	40
5.3.3.5	40
5.3.4	41
5.3.4.1	41
5.3.4.2	44
5.3.4.3	46
5.3.4.4	46
5.3.4.5	46
5.3.5	46
5.3.5.1	46
5.3.5.2	53
5.4	54
5.4.1	54
5.4.2	54
5.4.3	55
5.4.3.1	55
5.4.3.2	59
5.4.3.3	64
5.4.3.4	67
5.5	69
5.5.1	69
5.5.2	70
5.5.3	71
5.5.3.1	72
5.5.3.2	72
5.5.3.3	73
5.5.3.4	73
5.5.3.5	73
6	74
6.1	74
6.2	74
6.3	75
6.4	75
7	84
7.1	84
7.2	84
7.4	84



	Page
8	89
8.1	89
8.2	89
9	90
9.1	90
9.2	90
9.3	90
9.3.1	90
9.3.2	94
10	95
10.1	95
10.2	95
11	96
11.1	96
11.2	96
11.3	96
11.3.1	96
11.3.2	97
11.3.3	97
11.4	97
REFERENCES	101
INDEX	105

## LIST OF FIGURES

Figure		Page
1	PHASE DIAGRAM OF WATER	14
2	ATMOSPHERIC STABILITY AND VERTICAL TEMPERATURE GRADIENT	32
3	DECISION TREE FOR MODEL SELECTION	34
4	SCHEMATIC DIAGRAM OF A CONTINUOUS POINT SOURCE	35
5	SCHEMATIC DIAGRAM OF A CONTINUOUS AREA SOURCE	37
6	LATERAL DIFFUSION, $\sigma_y$ , VERSUS DOWNWIND DISTANCE FROM SOURCE FOR PASQUILL'S TURBULENCE TYPES	38
7	VERTICAL DIFFUSION, $\sigma_z$ , versus DOWNWIND DISTANCE FROM SOURCE FOR PASQUILL'S TURBULENCE TYPES	39
8	VAPOUR EMISSION RATE vs LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES	43
9	NORMALIZED VAPOUR CONCENTRATION vs DOWNWIND DISTANCE	45
10	VAPOUR CONCENTRATION vs DOWNWIND DISTANCE	47
11	HAZARD ZONE MAPPING FOR WIND FROM 270°C	49
12	HAZARD ZONE MAPPING FOR WIND FROM 270°C $\pm$ 10°C	49
13	PLUME TRAVEL TIME vs TRAVEL DISTANCE	50
14	CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m <sup>3</sup> )	51
15	CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m <sup>3</sup> )	52
16	EXAMPLE OF A CARBON ADSORPTION CURVE	92

## LIST OF TABLES

Table		Page
1	K <sub>F</sub> FACTORS FOR ALIPHATIC AND ALICYCLIC ORGANIC COMPOUNDS	16
2	VOLUME INCREMENTS ( $v_i$ ) FOR COMMON ELEMENTS AND IONS	21
3	WEATHER CONDITIONS	44
4	MAXIMUM PLUME HAZARD HALF-WIDTH (for Ethylbenzene at 20°C)	48
5	SPREAD OF A HIGH VISCOSITY LIQUID ON A LOW VISCOSITY LIQUID	56
6	SPREAD OF A LOW VISCOSITY LIQUID ON A HIGH VISCOSITY LIQUID	57
7	MAXIMUM POOL RADIUS	68



## INTRODUCTION

The EnviroTIPS series of manuals was developed to fill a need for in-depth spill countermeasures and strategy planning information for top priority substances. Each manual is intended as a monograph containing information relevant to its behaviour, control, dispersion, effects, and cleanup of spills. The emphasis is on environmental effects, and the focus is on Canadian conditions from material, legislative and climatic standpoints. General principles of spill response are not discussed; rather, the available literature is summarized as it relates to a specific substance and to spills of that substance.

This manual is an introduction, outlining the intent and direction of each section; it provides the necessary theoretical bases for calculations included in each manual. In addition, the definitions of the terms appearing in EnviroTIPS manuals are given. The contents of the manuals are indicated by the following condensed table of contents:

Chapter	Heading	Sub-inclusions	Purpose
1	Summary		overview of response needs
2	Physical and Chemical Data	data; variations with temperature, pressure	comprehensive tabulation of physical/chemical data relevant to spill/emergency response
3	Commerce	manufacturers and processes; production levels; major transportation routes	overview of production levels, users, suppliers, volumes transported and routes
4	Materials Handling and Compatibility	containers and vessels; offloading; compatibility with materials	discussion of most common transportation vehicles and their properties
5	Contaminant Transport	leak nomograms; dispersion in air; behaviour on or in water; penetration into soil	specific calculations and models for transport of substance and dispersion in soil, air, and water

Chapter	Heading	Sub-inclusions	Purpose
6	Environmental Data	drinking water; aquatic toxicity; effect studies; degradation	data for estimating the degree of hazard of spills to the environment, usable as a guide to the cleanup requirements
7	Human Health	recommended exposure limits; irritation data; acute toxicity; chronic toxicity	for use in estimating the hazard to inhabitants near a spill and to cleanup personnel
8	Chemical Compatibility		guide to the hazards of mixtures of chemicals in a spill
9	Countermeasures	recommended handling procedure; cleanup and treatment; treatment processes; disposal; protective measures; specialized countermeasures equipment	cleanup guide; principles and hands-on practices based on theoretical and practical considerations
10	Previous Spill Experience		discussion of spills; illustrative of problems with each substance as a guide for future spills
11	Analytical Methods	in air, water and soil	guide to the selection of analytical methods based on spill conditions
12	References and Bibliography		

Each section is intended to cover as wide a range of conditions as possible, while at the same time offering information of immediate value for specific instances. A comprehensive literature search was undertaken and summarized for this work. Where information must be derived for each individual spill incident, as is the case with environmental dispersion modelling, theoretical bases appropriate for the broadest possible range of spill circumstances are provided, with guidance for their use. Where

example calculations or procedures are provided, the same conditions of climate and spill mass are used throughout the manuals so that hazard levels due to different substances may, if desired, be meaningfully compared.

Some mathematical relationships were used from literature, while other material has been prepared specifically for this series of manuals. As a result, some information appearing may differ from that in other spill literature. This is due to the use of different assumptions for these manuals, with the intent of considering conditions most appropriate to Canadian experience and practice.

No discussion has been provided on the organization, communications and logistics of response organizations. These manuals should serve as data sources for skilled response organizations already possessing appropriate training and infrastructure.

## 1 SUMMARY

### 1.1 Overview and Objectives

The summary in these manuals highlights those properties of a substance of most immediate relevance from a spill response standpoint. Where possible, quantitative information is given and properties of commercial materials are cited.

### 1.2 Selection and Presentation of Data

The emphasis in the presentation of the data has been to:

- a) identify the substance, by name, UN number, CAS number;
- b) indicate identifying markings (placard, label);
- c) state the most likely immediate problem; this is the first priority after the material has been identified;
- d) provide quantitative data on the most important physical properties;
- e) provide an indication of environmental concerns; where quantitative data are considered useful, they are provided; in general, a summary of routes of environmental threat and threatened species is more useful;
- f) indicate concerns relating to human health; primary focus is on the acute effect on those in the immediate vicinity, i.e., neighbours and response personnel;
- g) indicate first-response spill and fire control principles appropriate to the substance; these are necessarily general, since spill response is often best carried out on a site-specific basis; and
- h) indicate cleanup and countermeasure techniques suited to the substance; again, these are not site-specific; selection of the appropriate measures will depend on the conditions at the spill site and the surrounding environment.



## 2 PHYSICAL AND CHEMICAL DATA

### 2.1 Overview and Objectives

The purpose of these manuals is to cover all facets of spills and spill planning, therefore, it is desirable to list properties relevant to both immediate action needs and contingency planning. The need for such data as fire properties and liquid density is apparent from fire control and liquid containment standpoints. To predict dispersion in the environment and effects over a long-term period, more detailed data are required. Spreading on soil or water, for example, is controlled in part by density and viscosity, evaporation, heat of vaporization, and vapour pressure/temperature relationships; the toxic effect of a substance in water is controlled by its solubility.

### 2.2 Information Sources

Data are derived primarily from the available literature, and to a lesser degree from responses of companies manufacturing the materials. Only a few values were verified experimentally; where values for a property conflicted, the best documented value was used. Where values are in question, the literature referenced should be consulted. All property values are presented in International System of Units (SIU), where possible. Some values, especially in the modelling portions, are presented in the cgs system. In some cases, a graphic presentation of data is useful; for instance, vapour pressure versus temperature.

### 2.3 Special Cases

Clarification of several definitions was required in order that use of terminology be consistent throughout the series. In many cases, a term has a variety of meanings according to the user. For consistency in the reports, the terms are used as follows:

#### 2.3.1 Fire Properties.

Flammable: having a closed cup flash point below 37.8°C (100°F).

Combustible: having a closed cup flash point over 37.8°C.

Noncombustible: neither flammable nor combustible; does not burn in air.

In these manuals, "flammable" limits refer to limits for supporting combustion; "explosive" limits refer to limits for detonation.

**2.3.2 Solubility.** The sources surveyed for data used various scales to describe solubility. At one extreme, materials soluble in the range of 0.02 to 1 g/100 mL were

considered soluble, and those below 0.02 g/100 mL, insoluble. At the other extreme, a value over 25 percent was considered "soluble", and a value under 25 percent was considered "slightly soluble". In this report, the following convention is used:

Miscible:	>100 g/100 mL
Very soluble:	50 to 100 g/100 mL
Soluble:	10 to 50 g/100 mL
Moderately soluble:	1 to 10 g/100 mL
Slightly soluble:	0.1 to 1 g/100 mL
Insoluble:	<0.1 g/100 mL

Data received in other scales have been converted to this scale. It is recognized that, in cases of extreme toxicity to aquatic life, some "insoluble" materials dissolve sufficiently to pose a threat. The primary use of this scale, however, is in considering mass transport in water. It is not intended for use as an input to aquatic toxicity estimation; in cases of even moderate toxicity to aquatic life, materials soluble to the extent of 0.1 g/100 mL or 1000 mg/L, dissolve sufficiently to pose a threat.

#### 2.4 Glossary of Chemical and Physical Terms

Antoine Vapour Pressure Equation

an expression of the form:

$$\log V = A + \frac{B}{T} + \frac{C}{T^2}$$

where A, B and C are constants and are different for each substance, T is the temperature and V is the vapour pressure; for some substances, the vapour pressure equation is well established and has been given in the EnviroTIPS manuals

Atomic Weight

the relative weight of an element as determined from the total number of protons and neutrons; this value is based on the assignment of 12.000 to carbon

Autoignition Temperature

the minimum temperature at which a substance will ignite without a flame or spark being present

Azeotrope

a liquid mixture of two or more substances which behaves like a single substance in that the vapour produced by evaporation has the same composition as the liquid; azeotropes are also called "constant boiling mixtures"

Behaviour in a Fire	any characteristic behaviour that might significantly increase the hazard presented by the burning material (e.g., dense smoke, flammable vapours, toxic smoke, possibility of polymerization or explosion)
Boiling Point	the temperature at which the material boils at 101.3 kPa atmospheric pressure; in some cases, the pressure at which a material boils may be given, especially where boiling is not observed at atmospheric pressure
Bulk Density	the weight of a unit volume of powder or aggregate material, also known as "apparent density"
Burning Characteristics	description of flame characteristics (documented only for materials with unusual flame characteristics)
Burning Rate	the rate (in millimetres per minute) at which the depth of a pool of liquid decreases as the liquid burns
Coefficient of Thermal Expansion	the rate at which the dimensions of a material change with changing temperature; expressed as either linear or volume coefficient (cubical) of thermal expansion
Compressibility Factor	the amount a liquid, gas or solid can be compressed before it changes state; the compressibility factor is usually expressed as $\gamma$ , or the ratio of the specific heats $C_p/C_v$
Constituent Components of Typical Commercial Grade (% each)	typical product purity for single-component materials or components of mixtures, including added stabilizers and inhibitors
Critical Pressure	the vapour pressure of a substance at its critical temperature
Critical Temperature	the temperature above which a substance cannot be condensed from gas to liquid however high the applied pressure
Decomposition Temperature	the temperature at which the material breaks down to simpler substances
Deflagration Point	temperature at which rapid autocombustion of particles of an explosive material occurs as a surface phenomenon; a property of low explosives
Density	the mass of the material contained within a unit volume at the specified temperature

Detonation Point	temperature at which extremely rapid, self-propagating decomposition of an explosive accompanied by a high pressure temperature wave occurs
Detonation Velocity	velocity at which the explosion shock wave propagates in the material
Dielectric Constant	the index of the ability of a substance to resist the transmission of an electrostatic force; the lower the value, the greater the resistance; at 20°C, air has a value of 1, water has a value of 80
Diffusivity	the rate at which molecules of the material diffuse through still air or water
Dipole Moment	a measure of the charge separation on a molecule; specifically, it is the distance between the positive and negative charges multiplied by the quantity of the charge
Dissociation Constant	the degree to which an ionic molecule dissociates in a medium (usually water)
Distillation Range	the temperature range between which a certain fraction boils off; the distillation range is only applicable to mixtures
Electrical Conductivity	the amount of electricity passed by a specific volume of material or alternatively the inverse of the resistance to the passage of electricity
Enthalpy	can be translated in most cases as "heat" and is the available energy of a molecule or group of molecules
Entropy of Formation	the unavailable energy of a molecule due to the internal arrangement of atoms and their motions
Eutectic Composition	the weight percentage of the material which, in a mixture with another material (e.g., water), will yield a minimum freezing point
Evaporation Rate	the rate at which a liquid changes state to a gas; usually expressed as g/m <sup>2</sup> of liquid pool surface
Explosiveness	an indication of the susceptibility of the material to detonation by spark, shock, fire, etc.
Flame Speed	the velocity of propagation of the flame front
Flame Temperature	the maximum temperature attained by the flame during combustion of a substance

Flammability	a descriptive indication of the relative combustibility of the material
Flashback Potential	an indication of the ease or risk of flame propagation along a vapour path, usually back to the vapour source
Flash Point	the lowest temperature at which vapours above a volatile combustible substance will ignite in air when exposed to a flame; flash points are given as OC (open cup) or CC (closed cup), depending on the apparatus used to measure them
Free Energy of Formation	the total energy (enthalpy and entropy) required to form a molecule from its constituent atoms
Freezing Point	temperature at which the material changes from a liquid to a solid
Gibb's Energy of Formation	identical to free energy of formation
Heat capacity (constant pressure) ( $C_p$ )	the heat required to raise the material temperature by a specified amount under conditions of constant pressure; the value may be used to compute temperature rise of the material in a fire
Heat capacity (constant volume) ( $C_v$ )	the heat required to raise the material temperature by a specified amount under conditions of constant volume; can be estimated from $C_p$ and the $C_p/C_v$ ( $\gamma$ ) ratio of specific heats or the compressibility factor
Heat of Combustion	amount of heat liberated during combustion of the material
Heat of Crystallization	the amount of heat liberated when crystallization occurs
Heat of Decomposition	amount of heat liberated during or required to produce decomposition
Heat of Dilution	the amount of heat liberated or absorbed when a substance is diluted (usually in water)
Heat of Formation	the heat evolved or absorbed when a compound is formed from elements in their standard states at a specified temperature and pressure
Heat of Hydration	the heat evolved or absorbed when water becomes part of the crystalline structure
Heat of Polymerization	amount of heat liberated by the formation of a polymer

Heat of Solution	amount of heat liberated during or required to produce dissolution in water
Heat of Transition	the amount of heat liberated or absorbed when a substance moves from one state to another or from one form to another
Heat of Vaporization	amount of heat required to vaporize the material with no temperature change
Henry's Law Constant	<p>the ratio of the concentration of a substance in water and in the air directly above; Henry's Law constants can be calculated by:</p> $H = \frac{16 P M}{T S}$ <p>where H is the Henry's Law constant, P is the partial pressure (mm Hg), M is the molecular weight, T is the temperature (degrees Kelvin) and S is the solubility (ppm)</p>
Hygroscopicity	the ability of a substance to absorb moisture from the air
Ignition Temperature	taken as the autoignition temperature
Impact Sensitivity	the sensitivity of explosive materials to impacts or shocks
Interfacial Tension	see Liquid Interfacial Tension
Ionization Constant	the degree to which a substance ionizes or dissociates in water
Ionization Potential	the minimum energy required to remove an electron from an atom or molecule, thus making a positive ion; the measurement presented in EnviroTIPS is that for the gas phase and is given in eV (electron volts)
Latent Heat of Fusion	amount of heat required to melt the material with no temperature change
Latent Heat of Sublimation	amount of heat required to volatilize the solid material; can be estimated as the sum of the latent heats of vaporization and fusion
Lattice Energy (of a crystal)	the energy required to form or break a crystal structure
Lead Block Test	a test in which an explosive is detonated on a lead block; the amount of deformation is related to the energy released by the explosion

Liquid Interfacial Tension with Air	a measure of the force at the surface of a liquid that tends to shape liquid fragments into spherical drops; liquids with high surface tensions show less tendency to spread on flat surfaces
Liquid Interfacial Tension with Water	a measure of the forces existing at the interface between a liquid and water; approximately, it is the difference between the individual surface tension of the liquid and that of water with air; low values of the interfacial tension indicate that the chemical spreads readily on a water surface
Lower Explosive Limit	minimum concentration of material in air which can be detonated by spark, shock, fire, etc.
Lower Flammability Limit	minimum concentration of material in air which will support combustion on contact with a source of ignition
Melting Point	temperature at which the material changes from a solid to a liquid
Molar Volume	the volume occupied by one mole (weight in grams equivalent to its molecular weight) of a substance at a specified temperature and pressure (often standard conditions)
Molecular Weight	the sum of the atomic weights of the elements of a molecule
Octanol/Water Partition Coefficient	the ratio of the concentration of a material in the octanol phase to the concentration in the aqueous phase of a two-phase octanol/water system
Polymerization Expansion	the ratio of volumes occupied by a material after and before polymerization occurs
Polymerization Temperature	the temperature at which the material can react with itself to form polymers
Pour Point	the lowest temperature at which a liquid can be poured from a standard container
Refractive Index	ratio of the velocity of light in a vacuum to its velocity in the substance
Resistivity	the resistance that a cubic centimetre of the material offers to the passage of electricity
Saturated Vapour Density	the total weight occupied by the vapour in a defined space and at a set temperature; the saturated vapour density is the product of the density of the vapour times its vapour pressure

Saturation Concentration	<p>the vapour concentration of the material above which no further volatilization can take place; it can be computed from:</p> $C_s = 1315.12(R)^{-1} (P) (MW) (T)^{-1}$ <p>where <math>C_s</math> is the saturation concentration (<math>\text{mg}/\text{m}^3</math>); <math>R</math> is the Universal Gas Constant (<math>0.08205 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}</math>); <math>P</math> is the vapour pressure (<math>\text{mm Hg}</math>); <math>T</math> is the temperature (<math>\text{K}</math>) (<math>\text{Temperature } (^{\circ}\text{C}) + 273.16</math>); <math>MW</math> is the gram molecular weight of the material; 1315.12 is the conversion factor (from <math>\text{mm Hg}</math> to <math>\text{ppm}</math>)</p>
Solubility	the amount of a substance which can be dissolved in another substance at a given temperature
Specific Heat	see Heat Capacities
Specific Heat Ratio ( $C_p/C_v$ , $\gamma$ )	the ratio of the constant pressure over the constant volume heat capacities; this ratio is also known as the molar compressibility factor
Specific Gravity	ratio of the density of the material to that of water at $4^{\circ}\text{C}$ . If greater than 1, the material will sink in water; if less than 1, the material will float. Seawater has a specific gravity of 1.03
Standard Condition	a pressure of 101.1 kPa (1 atmosphere) and a temperature of $20^{\circ}\text{C}$
State	three states of material are solid, liquid or gas
Sublimation Point, Temperature	the temperature at which a material sublimates, i.e., becomes a gas directly from the solid state without becoming a liquid
Surface Tension	see Interfacial Tension.
Thermal Conductivity	the ability of the material to conduct heat across a temperature gradient; higher values reflect increasing amounts of heat transfer; lower values indicate better insulating properties
Transition Point, Temperature	the temperature at which a substance is converted from one state to another
Triple Point	the temperature at which all three states (solid, liquid and gas) are at equilibrium
Upper Explosive Limit	maximum concentration of material in air which can be detonated by spark, shock, fire, etc.
Upper Flammability Limit	maximum concentration of material in air which will support combustion on contact with a source of ignition



Vapour Density	the specific gravity of a vapour or gas as compared to air (equal to 1); a gas with a specific gravity of greater than 1 sinks in air; vapour density is a traditional expression that should be more properly referred to as vapour specific gravity
Vapour Pressure	the pressure of the vapour in equilibrium with the liquid at the specified temperature
Vapour Weight to Volume Conversion Factor	factor for conversion from ppm to $\text{mg/m}^3$ of vapour
Vapour Specific Gravity	the relative weight of a volume of vapour compared to that of air at the same temperature
Viscosity	the resistance of the material to flow at the specified temperature; higher values indicate thicker, slower-moving materials

## 2.5 Derivation of Phase Diagrams

**2.5.1 General Introduction.** Depending on the ambient conditions, a chemical substance can exist as a solid, liquid or vapour. The relationship between ambient conditions and the physical state of a substance is shown by the phase diagram for the substance. The example shown in Figure 1 is for water.

Pressure (P) is shown on the vertical axis and temperature (T) on the horizontal axis. The values of these two parameters determine the state of the substance. The simplest phase diagram consists essentially of three different lines, AB, AC and AD. Line AB represents the conditions under which the liquid and vapour are in equilibrium; line AC represents conditions for the solid in equilibrium with vapour; and line AD represents conditions for an equilibrium between solid and liquid. Point A on the phase diagram constitutes a triple point, where the three phases coexist in equilibrium ( $T = 0^\circ\text{C}$  and  $P = 0.67 \text{ kPa}$  for water). Regions indicated by "solid", "liquid" and "vapour" indicate the phases in equilibrium along each line.

On most phase diagrams,  $P_c$  and  $T_c$ , the critical pressure and critical temperature, are shown. The critical temperature is the temperature above which the vapour cannot be condensed to the liquid however high the applied pressure. The critical pressure is the vapour pressure at the critical temperature. Two symbols used are  $P_s$  and  $T_s$ , atmospheric pressure and atmospheric temperature,  $101.325 \text{ kPa}$  and  $20^\circ\text{C}$ , respectively. Both are considered to be "standard" conditions.

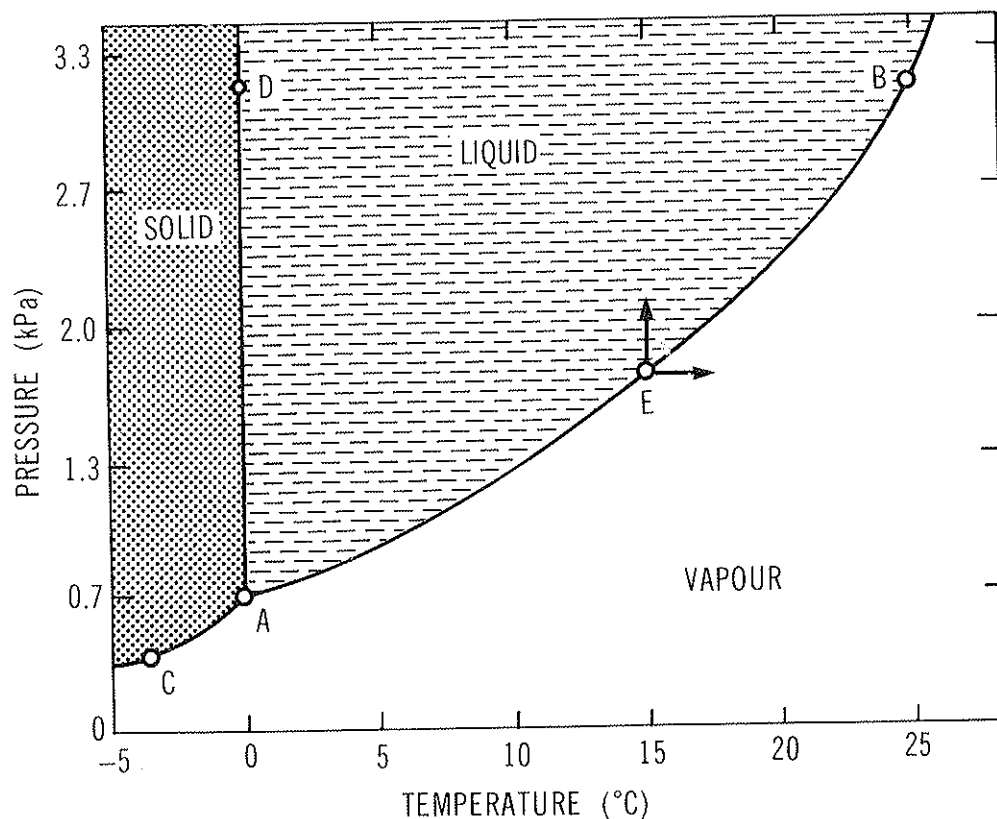


FIGURE 1 PHASE DIAGRAM OF WATER

With many substances in the "EnviroTIPS" series, complete experimental data are unavailable. However, mathematical expressions may be used to estimate the data necessary for phase diagrams quite accurately.

## 2.5.2 Methods for Estimating Phase Diagrams.

**2.5.2.1 Estimation of the liquid-vapour equilibrium.** The Antoine equation is the simplest relationship to use; however, it is applicable only over the normal liquid range. If this equation is used for temperatures below the melting point, the vapour pressure of the supercooled liquid, which is greater than the vapour pressure of the true "crystalline" solid, will be obtained.

The equation has many forms, depending upon the parameters known. The following is an example of an Antoine equation (the constants are found in literature; they are specified for different substances and temperature ranges):

$$\log P_v = A + \frac{B}{T} + C \log T + DT \quad (\text{Yaws 1974})$$

where  $P_v$  is the vapour pressure of the saturated liquid (mm Hg), and  $T$  is the temperature (in degrees Kelvin, K);  $A$ ,  $B$ ,  $C$  and  $D$  are correlation constants.

Example: The range of applicability for benzene is  $7.6^\circ\text{C}$  to  $289.4^\circ\text{C}$ . Calculate  $P_v$  (mm Hg) at  $20.0^\circ\text{C}$  given the Antoine constants (the experimentally measured vapour pressure at  $20^\circ\text{C}$  is 10.1 kPa):

$$A = 51.204$$

$$B = -3245.7$$

$$C = -16.403$$

$$D = 7.540 \times 10^{-3}, \text{ then}$$

$$P_v = 74.97 \text{ mm Hg} = 9.995 \text{ kPa}$$

If the constants  $A$ ,  $B$ ,  $C$  and  $D$  are not known, the following form of the Antoine equation may be used (Little 1981):

$$\ln P_{vp} = \frac{\Delta H_{vb} (T_b - C_2)^2}{\Delta Z_b R T_b^2} \left[ \frac{1}{(T_b - C_2)} - \frac{1}{(T - C_2)} \right]$$

where  $P_{vp}$  = vapour pressure (mm Hg)  
 $\Delta Z_b$  = compressibility factor at the boiling point (taken to be 0.97)  
 $T_b$  = boiling point, in degrees Kelvin  
 $C_2$  = constant  
 $T$  = temperature, in degrees Kelvin  
 $\Delta H_{vb}$  = latent heat of vaporization at the boiling point

The constant  $C_2$  can be estimated via Thomson's rule (Thomson 1959):

$$\begin{aligned} C_2 &= -18 + 0.19 T_b \\ &= -18 + 0.19 (353.25^\circ\text{K}) = 49.12 \end{aligned}$$

If the latent heat of vaporization at the boiling point is not known, it can be estimated by the Fishtine (1963) method. He modified the Kistiakovskii (1921) equation to obtain:

$$\frac{\Delta H_{vb}}{T_b} = K_F (8.75 + R \ln T_b)$$

where  $K_F$  = factor derived from a consideration of the dipole moments of polar and nonpolar molecules (Little 1981) (Table 1)

TABLE 1 K<sub>F</sub> FACTORS FOR ALIPHATIC AND ALICYCLIC\* ORGANIC COMPOUNDS

Compound Type	Number of Carbon Atoms (N) in Compound, Including Atoms of Functional Group											
	1	2	3	4	5	6	7	8	9	10	11	12 to 20
<b>HYDROCARBONS</b>												
n-Alkanes	0.97	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Alkane isomers				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Mono- and diolefins and isomers		1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.00
Cyclic saturated hydrocarbons			1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Alkyl derivatives of cyclic saturated hydrocarbons				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
<b>HALIDES (saturated or unsaturated)</b>												
Monochlorides	1.05	1.04	1.03	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01
Monobromides	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01
Monoiodides	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Polyhalides (not entirely halogenated)	1.05	1.05	1.05	1.04	1.04	1.04	1.03	1.03	1.03	1.02	1.02	1.01
Mixed halides (completely halogenated)	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Perfluorocarbons	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
<b>COMPOUNDS CONTAINING THE KETO GROUP</b>												
Esters		1.14	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Ketones			1.08	1.07	1.06	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Aldehydes	-	1.09	1.08	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
<b>NITROGEN COMPOUNDS</b>												
Primary amines	1.16	1.13	1.12	1.11	1.10	1.10	1.09	1.09	1.08	1.07	1.06	1.05**
Secondary amines		1.09	1.08	1.08	1.07	1.07	1.06	1.05	1.05	1.04	1.04	1.03**
Tertiary amines			1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Nitriles	-	1.05	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
Nitro compounds	1.07	1.07	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
<b>SULPHUR COMPOUNDS</b>												
Mercaptans	1.05	1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Sulphides		1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
<b>ALCOHOLS</b>												
Alcohols (single-OH group)	1.22	1.31	1.31	1.31	1.31	1.30	1.29	1.28	1.27	1.26	1.24	1.24**
Diols (glycols or condensed glycols)		1.33	1.33	1.33	1.33	1.33	1.33	1.33				
Triols (glycerol, etc.)			1.38	1.38	1.38							
Cyclohexanol, cyclohexyl methyl alcohol, etc.						1.20	1.20	1.21	1.24	1.26		
<b>MISCELLANEOUS COMPOUNDS</b>												
Ethers (aliphatic only)		1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Oxides (cyclic ethers)		1.08	1.07	1.06	1.05	1.05	1.04	1.03	1.02	1.01	1.01	1.01

\* Carbocyclic or heterocyclic compounds having aliphatic properties.

\*\* For N = 12 only, no prediction is made for K<sub>F</sub> where N > 12.

## Notes:

1. Consider any phenyl group as a single carbon atom.
2. K<sub>F</sub> factors are the same for all aliphatic isomers of a given compound. For example, K<sub>F</sub> = 1.31 for n-butyl alcohol, i-butyl alcohol, t-butyl alcohol, and s-butyl alcohol.
3. In organometallic compounds, consider any metallic atom as a carbon atom.
4. For compounds not included in this table, assume K<sub>F</sub> = 1.06.

$R$  = gas constant (1.987 cal/(mole•K))

$T_b$  = boiling point, degrees Kelvin

For benzene,  $K_F = 1.00$  and  $T_b = 353.25$  K; therefore,

$$\frac{\Delta H_{vb}}{T_b} = 1.00 (8.75 + 1.987 \text{ cal/(mole}\cdot\text{K)} \ln 353.25^\circ\text{K})$$

$$= 20.41 \text{ cal/(mole}\cdot\text{K)}$$

Therefore, at  $20^\circ\text{C}$ :

$$\ln P_{vp} = \frac{20.41 \text{ cal/(mole}\cdot\text{K)} (353.25^\circ\text{K} - 49.12^\circ\text{K})^2}{0.97 \times 1.987 \text{ cal/(mole}\cdot\text{K)} \times 353.25^\circ\text{K}} \left[ \frac{1}{(353.25^\circ\text{K} - 49.12^\circ\text{K})} - \frac{1}{(293.15^\circ\text{K} - 49.12^\circ\text{K})} \right]$$

$$\ln P_{vp} = -2.24564$$

$$P_{vp} = 0.10586 \text{ atm} \times 101.325 \text{ kPa/atm} = 10.73 \text{ kPa}$$

This compares well with the measured value (10.1 kPa). Note that the only experimental information used is the boiling point.

**2.5.2.2 Estimation of the solid-vapour equilibrium.** The previous equations assumed that  $\Delta H_v/\Delta Z_b$  was temperature-independent, an assumption which may result in inaccurate estimations, especially below the melting point. However, the following modified Watson correlation takes the temperature dependence of  $\Delta H_v$  into consideration (Watson 1943):

$$\ln P_{vp} = \frac{\Delta H_{vb}}{\Delta Z_b R T_b} \left[ 1 - \frac{(3 - (2 T_{pb}))^m - 2m (3 - (2 T_{pb}))^{m-1} \ln T_{pb}}{T_{pb}} \right]$$

where  $T_{pb} = T/T_b$  (the ratio of the temperature of interest to the boiling point of the substance, in degrees Kelvin)

$m$  = constant, depending upon the physical state at the temperature of interest.

For all liquids  $m = 0.19$ ,

$T_{pb} > 0.6$ ;  $m = 0.36$

$0.6 > T_{pb} > 0.5$ ;  $m = 0.8$

$T_{pb} < 0.5$ ;  $m = 1.19$

So at 20°C, using the Fishtine method (Fishtine 1963):

$$\frac{\Delta H_{vb}}{T_b} = 20.41 \text{ cal}/(\text{mole} \cdot \text{K})$$

where  $m = 0.19$  (benzene is a liquid at 20°C)

$$T_{pb} = \frac{293.15\text{K}}{353.1\text{K}} = 0.830$$

$$\ln P_{vp} = \frac{20.41 \text{ cal}/(\text{mole} \cdot \text{K})}{0.97 \times 1.987 \text{ cal}/(\text{mole} \cdot \text{K})} \left[ \frac{1 - (3-2(0.83))^{0.19}}{0.83} - 2m(3-2(0.83)) - 0.81 \ln 0.83 \right]$$

$$\ln P_{vp} = -2.307$$

$$P_{vp} = \frac{0.0995 \text{ atm} \times 101.325 \text{ kPa}}{\text{atm}} = 10.09 \text{ kPa}$$

This relationship can also be used with great accuracy over the normal liquid range.

**2.5.2.3 Estimation of the solid-liquid equilibrium.** The variation of the pressure with temperature can be estimated using the Clapeyron equation (Castellan 1971):

$$\frac{dp}{dT} = \frac{\Delta S_{\text{fusion}}}{\Delta V_{\text{fusion}}} = \frac{\Delta H_{\text{fusion}}}{T_m \Delta V_{\text{fusion}}} = \frac{\Delta S_f}{\Delta V_f} = \frac{\Delta H_f}{T_m \Delta V_f}$$

where

$\Delta H_f$  = latent heat of fusion

$\Delta V_f$  = volume of liquid - volume of solid (near the melting point)

$\Delta S_f$  = entropy of fusion at the melting point

$T_m$  = melting point (degrees Kelvin)

$\frac{dp}{dT}$  = rate of change of pressure with temperature

The latent heat of fusion may be obtained from various sources. However, values for the densities of the solid and the liquid at various temperatures, necessary to derive molar volume, are often difficult to locate.

The liquid density can be estimated with Bhirud's method (Bhirud 1978):

$$\rho_l = \frac{MP_c}{Rte^{a+wb}}$$

where  $\rho_l$  = density of the liquid  
 $M$  = molecular weight (78.11 g/mole for benzene)  
 $P_c$  = critical pressure (48.3 atm for benzene)  
 $R$  = gas constant (82.04 cm<sup>3</sup> atm/(mole·K))  
 $w$  = acentric factor (measure of the sphericity of the molecule)

The latter can be calculated by the following equation developed by Edminster (Reid 1977):

$$w = \frac{3}{7} \left[ \frac{T_{br}}{1 - T_{br}} \right] \log P_c - 1$$

where  $T_{br} = \frac{T_b}{T_c}$

$T_b$  = boiling temperature

$T_c$  = critical temperature

$P_c$  = critical pressure

$$a = \text{constant} = 1.39644 - 24.076 Tr + 102.615 Tr^2 - 255.719 Tr^3 + 355.805 Tr^4 - 256.671 Tr^5 + 75.1088 Tr^6$$

$$b = \text{constant} = 13.4412 - 135.743 Tr + 533.380 Tr^2 - 1091.453 Tr^3 + 1231.43 Tr^4 - 728.227 Tr^5 + 176.737 Tr^6$$

where  $Tr = \frac{T}{T_c}$

For benzene at 280.15K:

$$T_{br} = \frac{353.25K}{562.09K} = 0.62846$$

$$w = \frac{3}{7} \frac{0.62846}{0.37154} \log 48.3 \text{ atm}^{-1} = 0.221$$

$$Tr = \frac{280.15K}{562.09K} = 0.49841$$

so  $a = -1.5599$

and  $b = -0.54866$

so 
$$\rho_l = \frac{78.11 \times 48.3}{82.04 \times 280.15K \times e} - 1.5599 + (0.221 \times -0.54866)$$

$\rho_l = 0.8818 \text{ g/mL}$

The density of the solid near the melting point can be estimated using the following equation (Little 1981):

$$\rho_s = \frac{M \times 1.660}{V_s}$$

where  $\rho_s$  = density of the solid

$M$  = molecular weight

$V_s$  = calculated crystal volume for a single molecule ( $\text{\AA}^3/\text{molecule}$ )

$$V_s = \sum_i m_i v_i$$

where  $v_i$  = unit volume of element  $i$  (Table 2)

$m_i$  = number of atoms of element  $i$  in molecule

This equation is the additivity method of Immirzi and Perini. It must be used with caution because the following restrictions apply:

- 1) Crystals that have a structural disorder or are not solids at room temperature are excluded.
- 2) Crystals may not contain molecules of solvent, with the exception of water.
- 3) Only the elements H, C, O, N, S, F, Cl, Br, I, Na, K and Rb are considered.
- 4) Cyclic compounds are limited to derivatives of benzene and naphthalene.

So for benzene, from Table 2 (Little 1981):

$$m_i \times v_i$$

Benzene = 1 Benzene frame

$$(\text{Carbons only}) = 1 \times 75.2 = 75.2$$

$$6 \text{ Hydrocarbon atoms} = 6 \times 6.9 = 41.4$$

$$V_s = \sum_i m_i v_i$$

$$V_s = (1 \times 75.2) + (6 \times 6.9) = 116.6 \text{ \AA}^3$$



TABLE 2 VOLUME INCREMENTS ( $v_i$ ) FOR COMMON ELEMENTS AND IONS\*

Element or Ion	$v_i$ ( $\text{\AA}^3$ )	Std. Error $\sigma$	No. of Contributors
-H	6.9	0.4	5228
=C=	15.3	0.7	74
-C	13.7	0.6	453
C	11.0	0.9	1165
=O	14.0	0.5	649
-O-	9.2	0.5	468
N	16.0	1.3	30
N	12.8	0.8	68
N	7.2	0.8	354
S	23.8	0.9	92
-F	12.8	1.5	14
-Cl	26.7	0.5	134
-Br	33.0	0.5	120
-I	45.0	1.3	26
Cl <sup>-</sup>	28.9	1.5	39
Br <sup>-</sup>	39.3	1.5	20
I <sup>-</sup>	56.6	2.5	11
Na <sup>+</sup>	13.6	2.2	16
K <sup>+</sup>	27.3	1.6	32
Rb <sup>+</sup>	34.1	2.2	15
H <sub>2</sub> O	21.5	0.8	68
Benzene frame (carbons only)	75.2	2.5	443
O-H ... O hydrogen-bond	-2.6	0.7	206
N-H ... O hydrogen-bond	-2.8	0.5	152
N-H ... N hydrogen-bond	-0.3	1.7	11
Non-aromatic rings (rough est.)	-3.0		

\* different coordination numbers are considered for C, N and O

$$\begin{aligned}
 \text{And since: } \rho_s &= \frac{1.660 \times M}{V_s} \\
 &= \frac{1.660 \times 78.11}{116.6} = 1.1 \text{ g/cm}^3
 \end{aligned}$$

Now that the densities of both the solid and the liquid are known,  $\Delta V_f$  may be estimated:

$$\Delta V_f = V_{\text{liquid}} - V_{\text{solid}} = \left[ \frac{1}{0.88 \text{ g/cm}^3} - \frac{1}{1.11 \text{ g/cm}^3} \right] \times 78.11 \text{ g/mole}$$

$$\Delta V_f = 18.39 \text{ cm}^3/\text{mole}$$

All the unknown parameters have been estimated and can now be used to estimate  $dP/dT$  using the Clapeyron equation:

$$\begin{aligned} \frac{dP}{dT} &= \frac{\Delta H_f}{\Delta V_f T_m} = \frac{2350.03 \text{ cal/mole}}{278.53\text{K} (18.39 \text{ cm}^3/\text{mole})} \\ &= 0.4588 \text{ cal}/(\text{cm}^3 \cdot \text{K}) \end{aligned}$$

$$= 1920.5 \frac{\text{kPa}}{^\circ\text{C}}$$

This is the slope of the solid-liquid equilibrium line. (The pressure must be increased by 1920.5 kPa to increase the melting point by 1 degree Celsius.)

### 3 COMMERCE AND PRODUCTION

This section provides an overview of the significance of each substance from the standpoints of the volume of production, the location of producers, the location of users, and the transportation routes. This information is of value in assessing the potential magnitude and frequency of incidents involving these substances. A knowledge of transportation routes will identify the areas to be covered by contingency plans or the expansion of available contingency services or preparedness.

A brief discussion on the production of each substance has been included to indicate the nature of the processes and equipment involved. This will aid in planning for incidents involving manufacturing facilities as well as transportation incidents.

Process descriptions are based on information volunteered by companies manufacturing each material. Where company information was unavailable, literature sources were used.

Where possible, the commercial grades shipped have been identified, so that spill behaviour and hazards may be correctly anticipated. These data have been obtained from manufacturers and other secondary sources. Volumes of production and use are primarily derived from data in industry publications and information services. Forecasts of future development have been derived from industry publications and producers' statements, considered to be best estimates at the time.

## **4 MATERIAL HANDLING AND COMPTABILITY**

### **4.1 Overview and Objectives**

Section 4 of each EnviroTIPS manual tabulates and discusses information on each substance pertaining to containers and transportation vessels, off-loading, and compatibility with materials of construction.

### **4.2 Information Sources**

A considerable body of data is available for railway tank cars, in contrast to the limited information available relating to tank trucks, portable tanks, drums and cylinders. Transport regulations and tank car manufacturers' literature were the prime data sources. Included in the information review were brochures from National Steel Car, Procor ACFX Railcar Services, and GATX. The Canadian Transport Commission and the Department of Transportation (U.S.) specification numbers for rail cars transporting each chemical were obtained from regulations or the tank car manufacturers, and from other sources such as the Handbook for Compressed Gases, data from the Chemical Manufacturers Association (formerly Manufacturing Chemists Association), and the chemical manufacturers themselves. Textbooks and various chemical trade associations were a useful source of specific transportation data for such chemicals as chlorine.

Information relating to tank motor vehicles as a transportation method for various chemicals was more difficult to obtain. Most useful information came from tanker manufacturers such as Fruehauf, Hutchinson and GATX. Some data from the chemical manufacturers, spill disposal contractors and the National Truck Association were also helpful. Most specification numbers for tank trucks were obtained from the Chemical Manufacturers Association and the Handbook of Compressed Gases.

Drums and cylinders were investigated using the Transportation of Dangerous Goods Code, the Chemical Manufacturers Association, the Handbook of Compressed Gases, and the chemical manufacturers.

Data related to precautions prior to off-loading and actual off-loading methods originated with pamphlets from the chemical manufacturers and booklets from the Chemical Manufacturers Association. Some information from the railcar and road tanker manufacturers was also of assistance. Specifications for off-loading equipment were extracted principally from data by the chemical producers.

### **4.3 Selection and Presentation of Data**

Because of the large number of available information sources for materials of construction that are compatible with each of the fifty hazardous chemicals, a comparison of material manufacturers' data was required to ensure consistency among their material compatibility ratings. The lowest rating ("recommended", "conditional" or "not recommended") established by any manufacturer was applied to each material considered in the tabulations in each manual.

In addition to the charts, brochures and catalogues available from material manufacturers, independent data sources such as handbooks (Hydraulics Institute) and booklets (Chemical Manufacturers Association) were also used.

## 5 CONTAMINANT TRANSPORT

### 5.1 Introduction

The dispersion of materials through the environment and the degree of hazard posed by a spill depend largely on the physical state of the material (solid, liquid, or gas) and upon site-specific conditions (the geology/geography of the site, terrain, temperature, weather, population and spill-related variables). In this section, methodologies for predicting dispersion in air, water, and soil will be presented.

Generalized prediction models are developed for each medium, taking into account the physical and chemical properties of the substance. Where possible, the relationships between variables - puncture size versus leak rate, for instance - are presented graphically or by nomograms. In this way, the effects of several variables can be ascertained in a relatively small number of steps or graph readings.

Although it would be possible to derive relationships to describe dispersion behaviour in terms of many spill-related variables, in practice it is necessary to make certain simplifying assumptions. These serve to limit the number of variables in the spill models and to permit a useful (though not necessarily exact) estimate of dispersion behaviour in a reasonable time.

For example, the leakage from a tank is assumed to be under isothermal conditions. This assumption is not precisely correct but it is, under most conditions of interest, more precise than the adiabatic assumption. The isothermal assumption produces a worst-case scenario where a more rapid leakage is obtained.

### 5.2 Leak Nomograms

**5.2.1 Overview and Objectives.** The rate of discharge of contaminants in a spill is a primary determinant of the hazard posed from flammability or environmental toxicity. The nomograms presented in this section provide a quick and reasonably good estimate of spill rate from punctures of various sizes.

Although the nomograms consider leaks under a specific set of conditions, the model may be extended to wider ranges of temperature or pressure using the relationships developed in Section 5.2.3.

**5.2.2 Information Sources.** The leak nomograms for the EnviroTIPS series have been calculated using a rationale based on that presented in "Assessment Models in Support of the Hazard Assessment Handbook" (Raj 1974). Basic thermodynamic principles are used;

the assumptions made are that gases behave as ideal gases; that equilibrium thermodynamics apply; and that the venting system is isothermal.

**5.2.3 Selection of Conditions and Calculation of Data.** For simplicity and ease of comparison between manuals, the same conditions are generally considered throughout the series. These are:

Initial Tank Conditions:

ambient temperature = 40°C (to provide a worst case scenario for Canadian conditions)  
or standard shipping temperature for refrigerated materials

pressure = ambient, or vapour pressure of substance, whichever is greater

volume = 80 000 L unless a special car is normally used for the substance

mass = equivalent to standard loading of 80 000 L tank

**5.2.3.1 Size and location of puncture.** Two puncture locations are considered, top and bottom. Nomograms are prepared for discharge versus puncture size; examples given in individual manuals are calculated for top punctures of 250 mm equivalent diameter and bottom punctures of 150 mm diameter.

The model assumes thermodynamic equilibrium (which is not the case in a sudden puncture and fast release) and isothermal conditions, which is also unrealistic for fast release. The model does provide a worst case first approximation of a liquid or gas discharge.

**5.2.3.2 Liquid venting.** Liquid is vented when the puncture is below the liquid level. Then,

$$q = AC_d \rho_l \left( 2g H + \frac{2(P - P_a)}{\rho_l} \right)$$

where

$q$	= instantaneous liquid vent rate (g/s)
$H$	= height of liquid column above hole (cm)
$P$	= tank pressure (dynes/cm <sup>2</sup> or $10^4$ kPa)
$A$	= area of puncture (cm <sup>2</sup> )
$C_d$	= coefficient of discharge (0.8)
$\rho_l$	= density of liquid (g/cm <sup>3</sup> )
$g$	= acceleration due to gravity (cm/s <sup>2</sup> )
$P_a$	= atmospheric pressure (dynes/cm <sup>2</sup> )

The coefficient of discharge is dependent on the geometry of the puncture and the Reynolds number of discharge. Typical values range from 0.6 to almost 1.0. Accidental punctures will have a wide range of geometrics and Reynolds numbers; therefore, an average value of 0.8 was chosen.

As an example, consider a standard tank car (2.75 x 13.4 m) filled with carbon dioxide at -23°C, punctured on the bottom. The equivalent diameter of the hole is 150 mm. What is the instantaneous discharge for an internal pressure of 2200 kPa?

$$\begin{aligned} H &= 275 \text{ cm} \\ P &= 2200 \text{ kPa} = 2.2 \times 10^7 \text{ dynes/cm}^2 \\ A &= 177 \text{ cm}^2 \\ C_d &= 0.8 \\ \rho_l &= 1.04 \text{ gm/cm}^3 \\ g &= 980 \text{ cm/s}^2 \\ P_a &= 1.00 \times 10^6 \text{ dynes/cm}^2 \end{aligned}$$

The above equation produces a result of 951 kg/s, or approximately 915 L/s, compared to the graphical approximation of 900 L/s shown in the EnviroTIPS manuals.

**5.2.3.3 Gas venting or release.** Gas will be released when the hole in the tank is above the liquid level. The maximum limiting flow rate for gas release is during "choked" flow. This flow rate is:

$$q_v = C_d A P \sqrt{\left( \frac{KM}{RT} \right) \left( \frac{2}{K+1} \right)^{\frac{K+1}{K-1}}}$$

where

- $q_v$  = vapour venting rate
- $T$  = absolute temperature in the tank
- $M$  = molecular weight
- $R$  = universal gas constant
- $P$  = tank pressure
- $K$  = specific heat ratio for the vapour
- $C_d$  = coefficient of discharge
- $A$  = area of puncture



The criterion for choked flow is:

$$\frac{P}{P_a} > \left( \frac{K+1}{2} \right)^{\frac{K}{K-1}}$$

where  $P_a$  = atmospheric pressure

For unchoked flow:

$$\frac{P}{P_a} \leq \left( \frac{K+1}{2} \right)^{\frac{K}{K-1}}$$

and the flow rate becomes

$$q_v = C_d A \sqrt{2 P \rho_v \left( \frac{K}{K-1} \right) \left\{ \left( \frac{P_a}{P} \right)^{\frac{2}{K}} - \left( \frac{P_a}{P} \right)^{\frac{K+1}{K}} \right\}}$$

where  $\rho_v$  = density of vapour

#### 5.2.3.4 Thermodynamic relationships. If the tank contains only gas:

$$P = \frac{M R_v T}{V}$$

where  $M$  = molecular weight

$V$  = specific volume of tank,  $m^3/g$

The pressure decrease with venting can be calculated with this relationship for isothermal conditions. If liquid is present, under isothermal conditions,

$$P = P_{sat}(T) = a e^{\frac{-b}{T}}$$

where  $P_{sat}(T)$  = saturated vapour pressure at temperature  $T$

$a, b$  = constants

The vent rate is constant until the liquid is gone.

For example, consider a standard tank car filled with carbon dioxide at  $-23^\circ\text{C}$  punctured on the top, with the equivalent diameter of the hole equal to 250 mm. What is the instantaneous discharge for an internal discharge of 2200 kPa?

$$\begin{aligned}
 P_a &= 100 \text{ kPa} = 1.0 \times 10^6 \text{ dynes/cm}^2 \\
 P &= 2200 \text{ kPa} = 2.2 \times 10^7 \text{ dynes/cm}^2 \\
 A &= 491 \text{ cm}^2 \\
 C_d &= 0.8 \\
 K &= 1/[1 - (1.986/M \cdot \text{CPG})] = 1.30 \\
 M &= \text{molecular weight} = 44.01 \\
 \text{CPG} &= \text{heat capacity of vapour, cal/(g} \cdot ^\circ\text{C)} \\
 &= 0.194 \text{ cal/g at } -23^\circ\text{C}
 \end{aligned}$$

$$\frac{P}{P_a} = 22$$

$$\left(\frac{K+1}{2}\right)^{\frac{K}{K-1}} = 1.83$$

Therefore the flow is choked

$$\begin{aligned}
 R_v &= (\text{Universal gas constant/molecular weight}) \\
 &= 1.89 \times 10^6 \\
 C &= 3.89 \times 10^{-4}
 \end{aligned}$$

The discharge rate is 266 kg/s, compared with the graphical approximation of 250 kg/s from the EnviroTIPS manuals.

### 5.3 Dispersion in the Air

**5.3.1 Overview and Objectives.** The problem of the dispersion of hazardous gases in the atmosphere resulting from accidental releases is an important one. While the effects of a hazardous material in soil or water are neither immediate nor violent in most cases, the effects of its dispersion in air may be of immediate and drastic significance. A fire or explosion may devastate part of a city or town, perhaps killing many people; toxic vapours could cause numerous casualties in a matter of minutes or hours. Because air dispersion is much faster than water or soil dispersion, and because of the potential in many cases for flammability or inhalation of toxic or asphyxiant gases, air dispersion poses a much more immediate and urgent problem than dispersion in soil or water.

The goal of the hazardous vapour dispersion problem is to predict the extent of the flammable or toxic hazard zone downwind of a spill site under the prevailing

conditions. The main factors which determine the area that will be affected by the hazardous material are:

- a) the source configuration (the chemical and its mode release, the quantity released, the rate of release, and the total elapsed time of emission);
- b) the atmospheric conditions; and
- c) the terrain.

These factors must be considered in any estimation of contaminant dispersion in air. The objective of this section is to describe the dispersion models and associated techniques employed in the preparation of the dispersion predictions and nomograms for chemicals in the EnviroTIPS series.

**5.3.2 Information Needs and Sources.** In an accidental situation, obtaining good information quickly on the source configuration is usually one of the most difficult tasks. The mode of release depends on the chemical and how it is stored, and on the nature of the puncture. The puncture may be highly irregular in shape and can occur anywhere on the containing vessel (e.g., above or below the liquid level). A gas leak from a tank would act as a "point" source of vapour emissions, whereas a liquid leak spreading on a land or water surface and evaporating would act as an "area" source. Both of these types of sources would be of a "semi-continuous" nature, whereas a catastrophic failure (such as a BLEVE) would result in an "instantaneous" cloud (or "puff") source. An examination of actual accidents indicated that the latter case, in which a large amount of material is released in a short time, is clearly the most important (McQuaid, 1979).

The quantity of chemical released and the rate of release are important source parameters which are difficult to estimate accurately in actual incidents. Of critical concern are the vapour release rates to the atmosphere either directly from a container or by evaporation from a liquid pool. The CHRIS (1974) Hazard Assessment Handbook provides some guidance and data on source strength quantification for releases from certain vessels. Some data and suggested methods for computing evaporation rates from liquid pools are given by Esso (1972), Leinonen and McKay (1975) and Fleischer (1980). The foregoing touches only briefly on the source configuration problem which is considered to be an area requiring further research (McQuaid 1979).

Once hazardous gases are released into the atmosphere, their transport and dispersion are governed primarily by the strength and direction of the advecting wind and the level of turbulent motions, respectively. Although these can be highly variable and consequently difficult to predict, there are some practical ways of categorizing the

atmospheric conditions which indicate the atmosphere's capacity to disperse airborne contaminants.

Since the turbulent structure of the atmosphere is intimately related to the temperature structure and since it is much more difficult to measure atmospheric turbulence than to measure the accompanying vertical temperature gradients, diffusion (or air pollution) meteorologists frequently use the latter to identify atmospheric stability and dispersal capacity.

Figure 2 depicts various vertical temperature profiles and the three broad categories of atmospheric stability: unstable, neutral and stable conditions. The neutral condition has a temperature decrease with height of about  $10^{\circ}\text{C}/\text{km}$  (called the adiabatic lapse rate). In unstable conditions (corresponding to a larger temperature gradient), there is a high level of turbulence which rapidly diffuses pollutants; in stable conditions, turbulence levels are low, resulting in little diffusion of pollutants. Material emitted into a stable atmosphere will drift downwind as a thin undisturbed ribbon for many tens of kilometres. Consequently, a stable condition with light winds is of most concern when a hazardous material spill occurs.

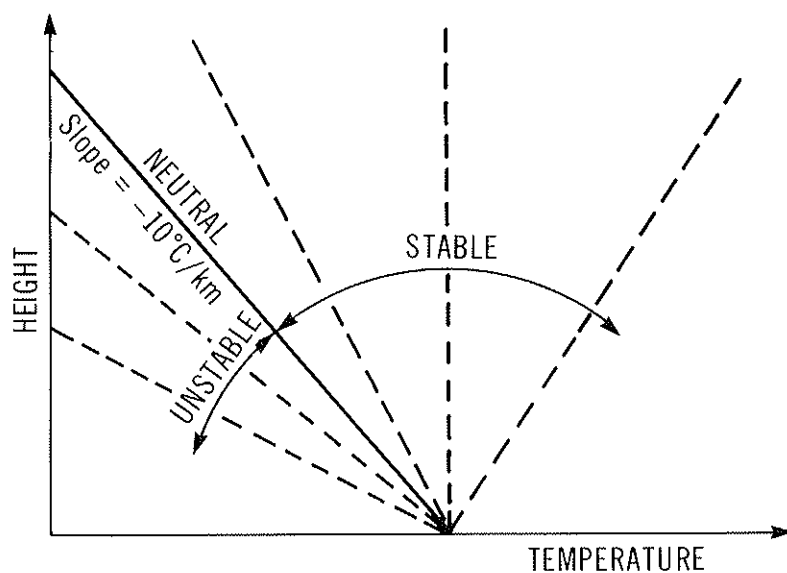


FIGURE 2      ATMOSPHERIC STABILITY AND VERTICAL TEMPERATURE GRADIENT

Terrain can influence the transport and diffusion of hazardous gases to a critical degree, especially for heavier-than-air gases (such as chlorine). Channelling of winds along valleys can lead to transport of gases with restricted lateral diffusion for

considerable distances. In light winds, the slope of the terrain has a significant influence on local airflow. Cooled topographic features in the case of a release of cold gas have resulted in slope flows; studies in a wind tunnel (Hall et al., 1974) and of an accident (Booj, 1979) reveal such effects. The trapping of dense gas in hollows is a serious topographic effect since heavy gas may persist in high concentrations in a hollow for a relatively long period of time.

**5.3.3 Dispersion Models.** Modelling the dispersion of hazardous vapour releases to the atmosphere is a complex problem. If simplifying assumptions are made about the physical and chemical behaviour of hazardous substances, the models presented here can be used to obtain estimates of vapour dispersion. These models are the ones most widely used in practice for concentration predictions. It is important that the user understand the inherent assumptions and limitations of the models before applying them to a particular situation.

For the purposes of the EnviroTIPS manuals, accidental vapour releases of chemicals transported by tank car or truck are considered to occur in two ways:

- a) direct vapour release (if the chemical is in a gaseous state, or if the top of a tank car or truck of liquid is punctured); and
- b) a liquid release (if the bottom of a tank car or truck of liquid is punctured) forming a pool on a ground or water surface, resulting in a vapour release to the atmosphere due to evaporation.

To estimate the vapour concentrations downwind of an accident site for determination of the flammability or toxicity hazard zone, the atmospheric dispersion of a contaminant vapour is modelled as a "puff" or "plume" according to the decision tree given in Figure 3. A gas leak from a tank is considered a semi-continuous point source, modelling as a plume, whereas the release of a large amount of gas over a very short time period of the order of seconds to minutes is considered an instantaneous point source modelled as a puff. For a release resulting in a pool of "slowly" evaporated liquid on a ground or water surface, the source is considered a continuous or semi-continuous area source suited to a plume model. For a release resulting of a highly volatile liquid (very rapid evaporation rate), the source is considered an instantaneous point source suited to a puff model.

The models presented here are based on the Gaussian models of Pasquill (1974) and others (Slade 1968; Turner 1970) and are utilized in the U.S. Coast Guard's Assessment Models in Support of the Hazard Assessment Handbook (Raj 1974; Rausch 1977). The

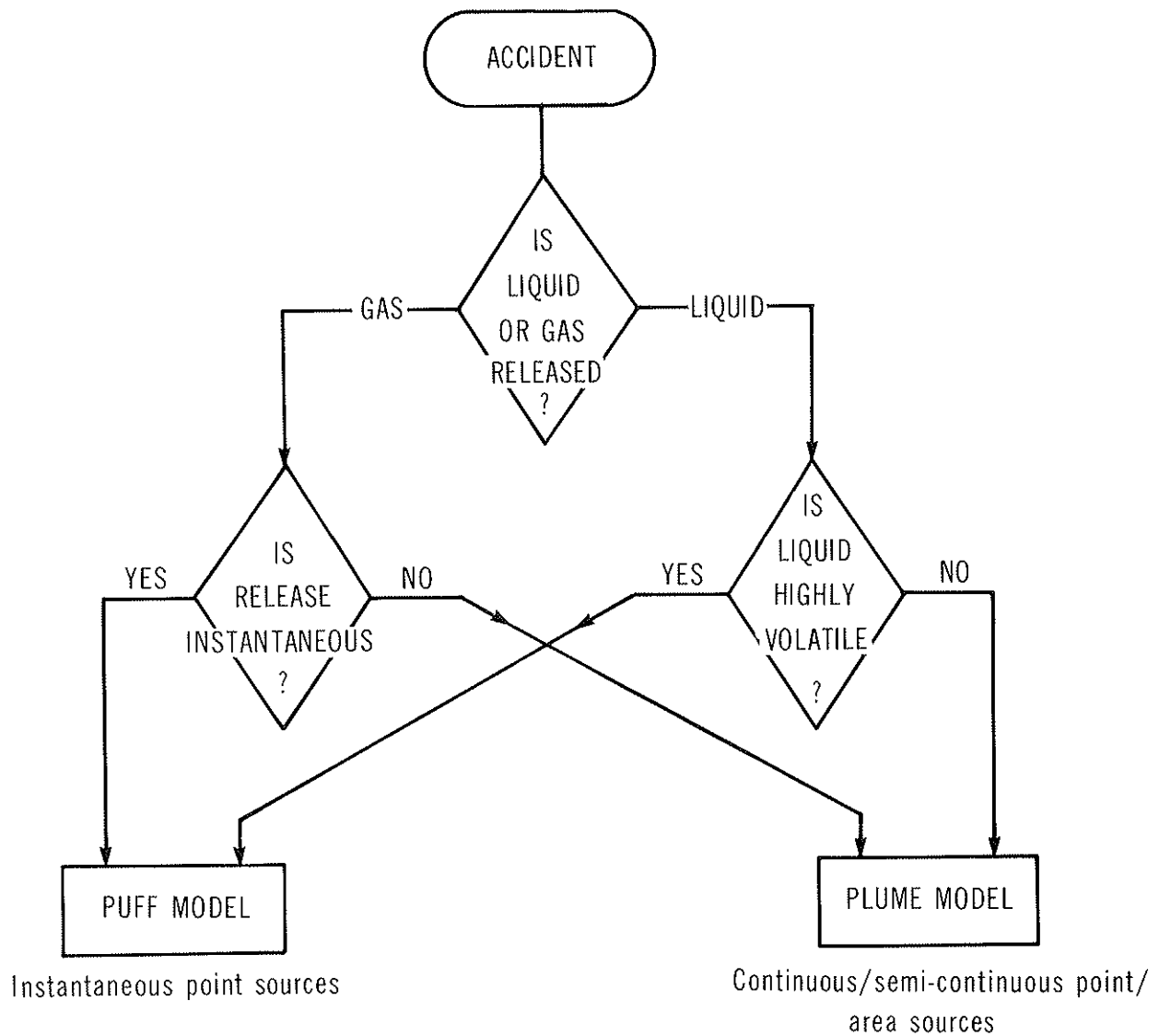


FIGURE 3 DECISION TREE FOR MODEL SELECTION

origin of the  $x$ ,  $y$ ,  $z$  coordinates is the ground directly beneath the source point or the centre of the area on the ground. The  $x$  direction is defined as the direction of the wind and  $z$  is the vertical direction (Figure 4).

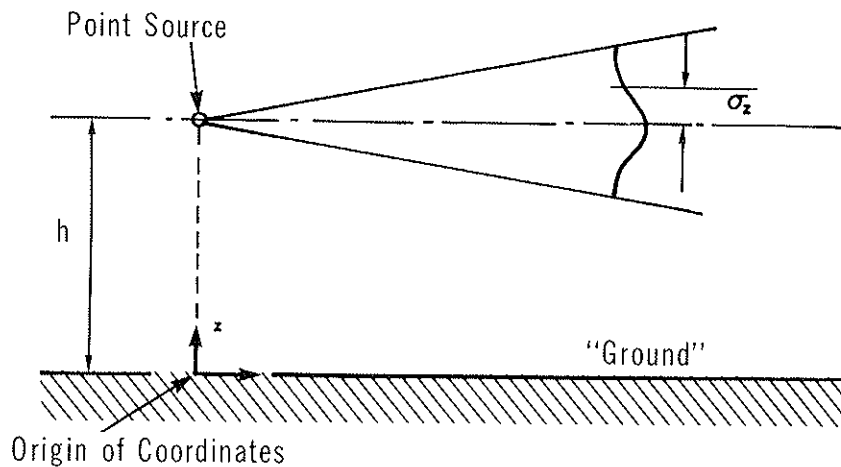


FIGURE 4 SCHEMATIC DIAGRAM OF A CONTINUOUS POINT SOURCE

**5.3.3.1 Assumptions.** In using the puff and plume equations described in the following pages, these assumptions are made:

- a) the vapour that is diffusing is neutrally buoyant; that is, there is no gross movement of the vapour cloud caused by either gravity or buoyancy;
- b) mixing with air is uniform throughout the vapour cloud;
- c) the concentration obtained is time-averaged;
- d) the wind is uniform throughout the vertical extent of the cloud;
- e) the terrain is flat (i.e., no terrain effects);
- f) the puff/plume is not depleted (e.g., by deposition); and
- g) the height of the puff or plume is not limited by a mixing layer.

**5.3.3.2 Input data required.** The following data are required:

- the atmospheric condition (stability of the atmosphere);
- the wind velocity and direction;

- the coordinates (with respect to the vapour source) of the point at which the concentration is to be calculated;
- the rate of vapour release for a "plume" release, total vapour release for a "puff" release; and
- the area of the source.

**5.3.3.3 Plume model.** For a vapour released continuously from a "point source" at a constant rate, the concentration at a point  $x, y, z$  downwind of the source at height  $h$ , is given by the following Gaussian Plume equation:

$$C(x,y,z,t) = \frac{Q}{2\pi U \sigma_y \sigma_z} \exp\left[-\frac{1}{2} \left(\frac{y}{\sigma_y}\right)^2\right] \left\{ \exp\left[-\frac{1}{2} \left(\frac{z-h}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2} \left(\frac{z+h}{\sigma_z}\right)^2\right] \right\} \quad (1)$$

for  $x \leq Ut$  and  $C(x,y,z,t) = 0$  for  $x > Ut$

where  $C$  = concentration of vapour ( $\text{g/m}^3$ )

$Q$  = rate of release of vapour ( $\text{g/s}$ )

$U$  = wind speed ( $\text{m/s}$ )

$x$  = downwind distance ( $\text{m}$ )

$y$  = crosswind distance ( $\text{m}$ )

$z$  = vertical distance ( $\text{m}$ )

$h$  = height of source ( $\text{m}$ )

$\sigma_y, \sigma_z$  = crosswind and vertical standard deviations of Gaussian concentration profile (see Figures 6 and 7) ( $\text{m}$ )

$t$  = time since release ( $\text{s}$ )

For plume centreline ( $y = 0$ ), at ground-level concentration ( $z = 0$ ) from a surface release ( $h = 0$ ), equation (1) reduces to:

$$\frac{Q}{\pi U \sigma_y \sigma_z} \quad x \leq Ut \quad (2)$$

$$C(x,0,0,t) = \begin{matrix} 0 & x > Ut \end{matrix} \quad (3)$$

This equation is the basis of the nomograms of normalized concentration ( $CU/Q$ ) versus downwind distance ( $x$ ) prepared for each chemical with continuous plume release characteristics.



For a continuous "area source", the rigorous procedure for obtaining the concentration at any point is to add the contribution from each infinitesimal point source in the area toward the concentration. This leads to the evaluation of an integral, which poses difficulties for practical applications. For estimating concentrations at large distances (greater than two equivalent diameters of the source area), the following simplified approach suffices in most practical cases.

The area is replaced by a "virtual point source" of the same total strength, but displaced upwind by a distance ( $x_y$ ) as shown in Figure 5. The distance  $x_y$  is a function of the concentration itself and is estimated by setting the crosswind extent (or diameter, ( $d$ )) of the area equal to the plume width ( $4.3 \sigma_{y0}$ , which defines the 10 percent concentration edge of a plume) downwind of the virtual point source; computing  $\sigma_{y0}$ , then using Figure 6, determining the distance  $x_y$  which corresponds to this rate of plume spread (Turner 1970). Hence, for area source calculations, substitute:

$$x' = x + x_y \quad (4)$$

If  $x_y$  is found to be less than 100 m (off the applicable range of Figure 6), or if use of  $\sigma_y$  vs  $x$  curves or relationships is not possible, the following rough approximation is suggested (Raj 1977):

$$x' = x + 5d \quad (5)$$

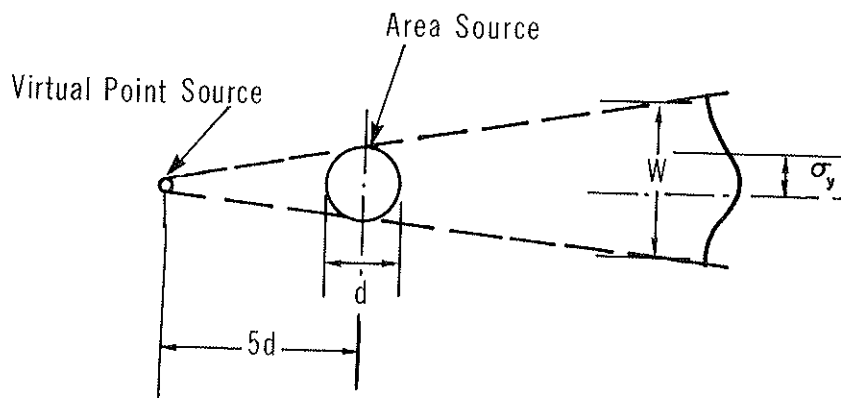


FIGURE 5 SCHEMATIC DIAGRAM OF A CONTINUOUS AREA SOURCE

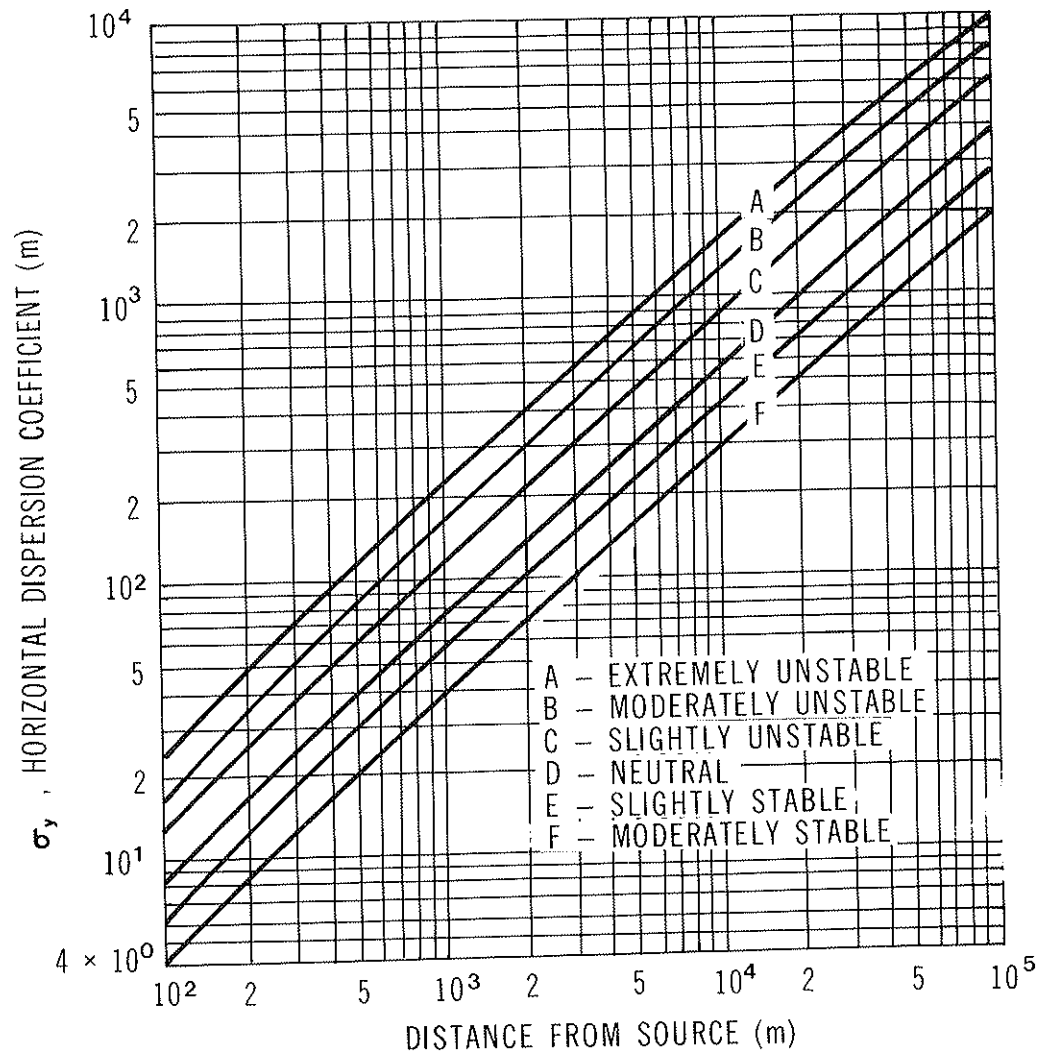


FIGURE 6

LATERAL DIFFUSION,  $\sigma_y$ , VERSUS DOWNWIND DISTANCE FROM SOURCE FOR PASQUILL'S TURBULENCE TYPES (Slade 1968)

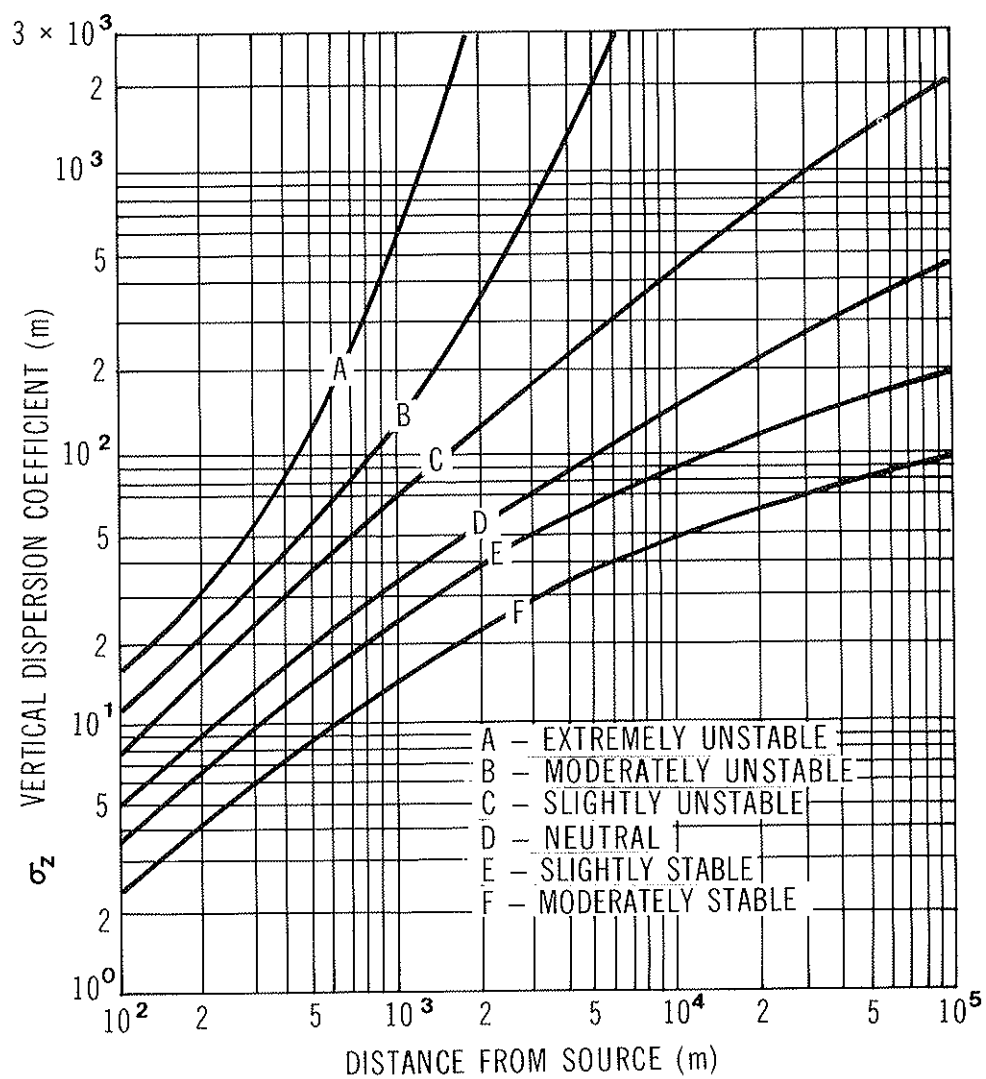


FIGURE 7

VERTICAL DIFFUSION,  $\sigma_z$ , VERSUS DOWNWIND DISTANCE FROM SOURCE FOR PASQUILL'S TURBULENCE TYPES (Slade 1968)

**5.3.3.4 Puff model.** The concentration at some point,  $x, y, z$  and time,  $t$ , downwind of an "instantaneously" released cloud (or puff), such as from a catastrophic failure of a pressurized gas container, is given by:

$$C(x, y, z, t) = \frac{2 Q_T}{(2\pi)^{3/2} \sigma_x \sigma_y \sigma_z} \exp\left[-1/2 \left(\frac{x-Ut}{\sigma_x}\right)^2\right] \exp\left[-1/2 \left(\frac{y}{\sigma_y}\right)^2\right] \exp\left[-1/2 \left(\frac{z-h}{\sigma_z}\right)^2\right] + \exp\left[-1/2 \left(\frac{z+h}{\sigma_z}\right)^2\right] \quad (6)$$

For concentrations along puff centreline ( $y = 0$ ), at ground level ( $z = 0$ ) from a surface release ( $h = 0$ ), equation (6) reduces to:

$$C(x, 0, 0, t) = \frac{4 Q_T}{(2\pi)^{3/2} \sigma_x \sigma_y \sigma_z} \exp\left[-1/2 \left(\frac{x - Ut}{\sigma_x}\right)^2\right] \quad (7)$$

where

$Q_T$	= total mass of vapour liberated (kg)
$C$	= concentration from an instantaneous (puff) release (kg/m <sup>3</sup> )
$U$	= wind speed (m/s)
$\sigma_x, \sigma_y, \sigma_z$	= puff diffusion (spread) coefficients (m)
$x, y, z$	= Cartesian coordinates with origin at the source. Wind taken to blow in positive $x$ -direction. The cross-wind coordinate is $y$ and $z$ is the vertical coordinate

Relationships for the puff diffusion coefficients are assumed to be the same as the Pasquill plume  $\sigma$ 's (with  $\sigma_x = \sigma_y$ ) in this work. Alternative relationships are given by Slade (1968). Equation (7) with these  $\sigma$ 's is the basis of normalized concentration ( $C/Q_T$ ) versus downwind distance ( $x$ ) calculations prepared for each substance with puff release characteristics.

**5.3.3.5 Plume/puff width.** The width of the part of a vapour plume or puff greater than a specified concentration ( $C^*$ ) at ground level can be derived by taking the ratio of the ground-level centreline concentration ( $C$ ) and the specified ground-level off-axis concentration ( $C^*$ ) at a point  $x$ . Taking the plume model as an example:

$$\frac{C^*}{C} = \exp\left[-1/2 \left(\frac{y}{\sigma_y}\right)^2\right] \quad (8)$$

and solving for  $y$  (the plume half width) gives:

$$y = \sqrt{2 \sigma_y} \sqrt{\ln \left( \frac{C}{C^*} \right)} \quad (9)$$

Therefore, the plume width  $W$  ( $=2y$ ) is given by:

$$w = 2 \sqrt{2 \sigma_y} \sqrt{\ln \left( \frac{C}{C^*} \right)} \quad (10)$$

Note, if  $C^*/C = 1/10$ , then  $W = 4.3 \sigma_y$

Since the plume and puff rates of spread (or  $\sigma$ 's) are taken as being the same, then the puff width is also described by equation (10).

**5.3.4 Vapour Dispersion Nomograms.** In this section, the following nomograms and tables are described:

- vapour emission rate from a liquid pool as a function of maximum pool radius;
- normalized vapour concentration as a function of downwind distance;
- plume/puff hazard half-width tabulations; and
- vapour plume/puff travel distance as a function of time elapsed since the spill.

**5.3.4.1 Vapour emission rate versus spill radius.** The evaporation rate for chemicals that form a liquid pool when spilled on a ground or water surface has been determined using the relationship of Stiver and Mackay (1982):

$$Q = KAPM/RT \quad (11)$$

where  $Q$  = evaporation rate (vapour release rate) (g/s)  
 $K$  = mass transfer coefficient (m/s)  
 $A$  = areas ( $m^2$ )  
 $P$  = vapour pressure (Pa)  
 $M$  = molecular weight (g/mole)  
 $R$  = gas constant, 8.314 (Pa)  $m^3/(mole \cdot K)$   
 $T$  = temperature (K)

The mass transfer coefficient  $K$  from Mackay and Matsugu (1973) is given by:

$$K = 0.0048 U^{0.78} d^{-0.11} Sc^{-0.67} \quad (12)$$

where  $U$  = wind speed (m/s)  
 $d$  = pool diameter (m)  
 $Sc$  = vapour phase Schmidt number (dimensionless)

For the purposes of this work, equation (12) is approximated by that given by Stiver and Mackay (1982):

$$K = 0.002 U^{0.78} \quad (13)$$

This approximation was obtained by setting  $d^{0.11}$  to unity and  $Sc$  to 2.7 (indicated as a typical value for hydrocarbons at environmental conditions). Using a value to  $U = 4.5$  m/s or 16 km/h, which is roughly the mean annual windspeed across Canada (Environment Canada 1975), equation (13) gives  $K = 0.0065$  m/s. Then, at a temperature of 20°C, the evaporation rate per square metre is found using equation (11):

$$E = \frac{Q}{A} = 2.65 \times 10^{-6} \times P \times M \text{ (g/m}^2\text{s)} \quad (14)$$

This formulation is considered to be applicable to pure chemicals with a boiling point (B.P.) no closer than 50 to 60°C above ambient, i.e., applicable to chemicals with a B.P. >70 to 80°C. Lower B.P. chemicals evaporate more slowly than predicted by equation (14) due to evaporative cooling effects. Because of this, the upper limit of applicability for equation (14) is an evaporation rate of about 20 g/(m<sup>2</sup>s). Equation (14) has been used as the basis for the vapour emission rate versus spill radius nomograms. An example for ethylbenzene is given in Figure 8.

The evaporation rate for temperatures other than 20°C was calculated based on the ratio of the vapour pressure of the chemical to that at 20°C and the ratio of the temperatures. Since the mass evaporation rate is directly proportional to vapour pressure and inversely proportional to absolute temperature, the evaporation rates at temperatures other than 20°C were calculated using the following equation:

$$E_t = E_{20^\circ\text{C}} \times \frac{P_t}{P_{20^\circ\text{C}}} \times \frac{293}{T_t} \quad (15)$$

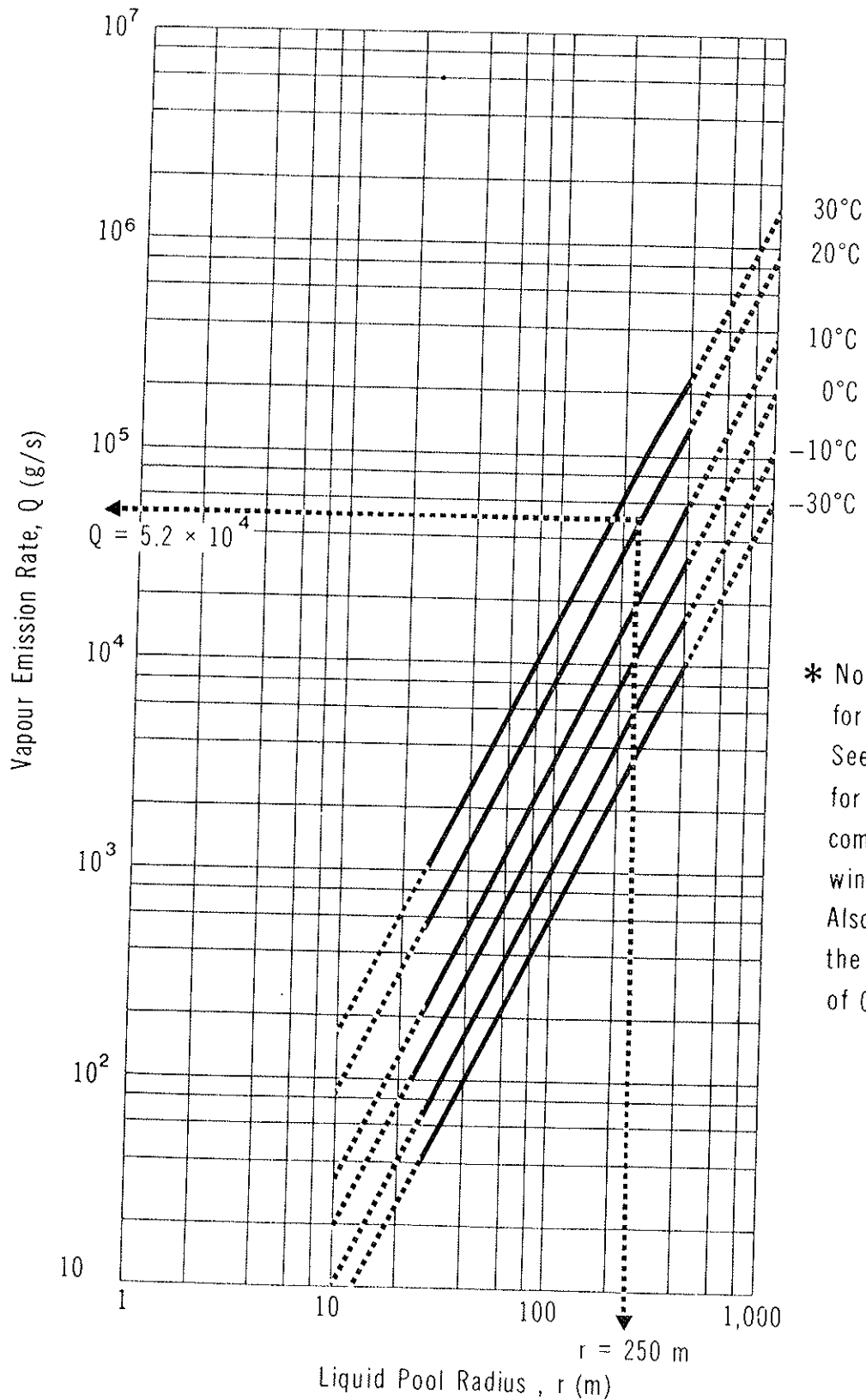
where the subscript "t" denotes the temperature at which the evaporation rate is desired.

Since the vapour emission rate versus liquid pool radius nomograms are based on an evaporation rate at a wind speed of 4.5 m/s, the nomograms can only be used to

FIGURE 8

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# VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES\*



\* Note: Nomogram applies for wind speed of 4.5 m/s. See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.2 to 70 tonnes.

provide an approximation of vapour emission rates at other wind speeds. To estimate the vapour emission rate for different wind speeds, the following equation can be used:

$$Q_U = Q_{4.5} \times \frac{U^{0.78}}{4.5^{0.78}} \quad (16)$$

where U denotes the wind speed at which the vapour emission rate is desired.

**5.3.4.2 Vapour concentration versus distance.** Figure 9 presents an example of the nomograms of normalized ground-level plume centerline concentration  $C_U/Q$  versus downwind distance  $x$  for atmospheric stability conditions D and F based on Equation 2. As indicated in Figures 6 and 7 (which are used for both the plume and puff models), atmospheric stability can be categorized into six groupings, from extremely unstable (A) to moderately stable (F). For practical purposes, the nomogram contains only D and F conditions since condition F is poorest for dispersing a vapour cloud and D is the most common in much of Canada. These weather conditions can be identified by an on-site observer as follows:

TABLE 3 WEATHER CONDITIONS

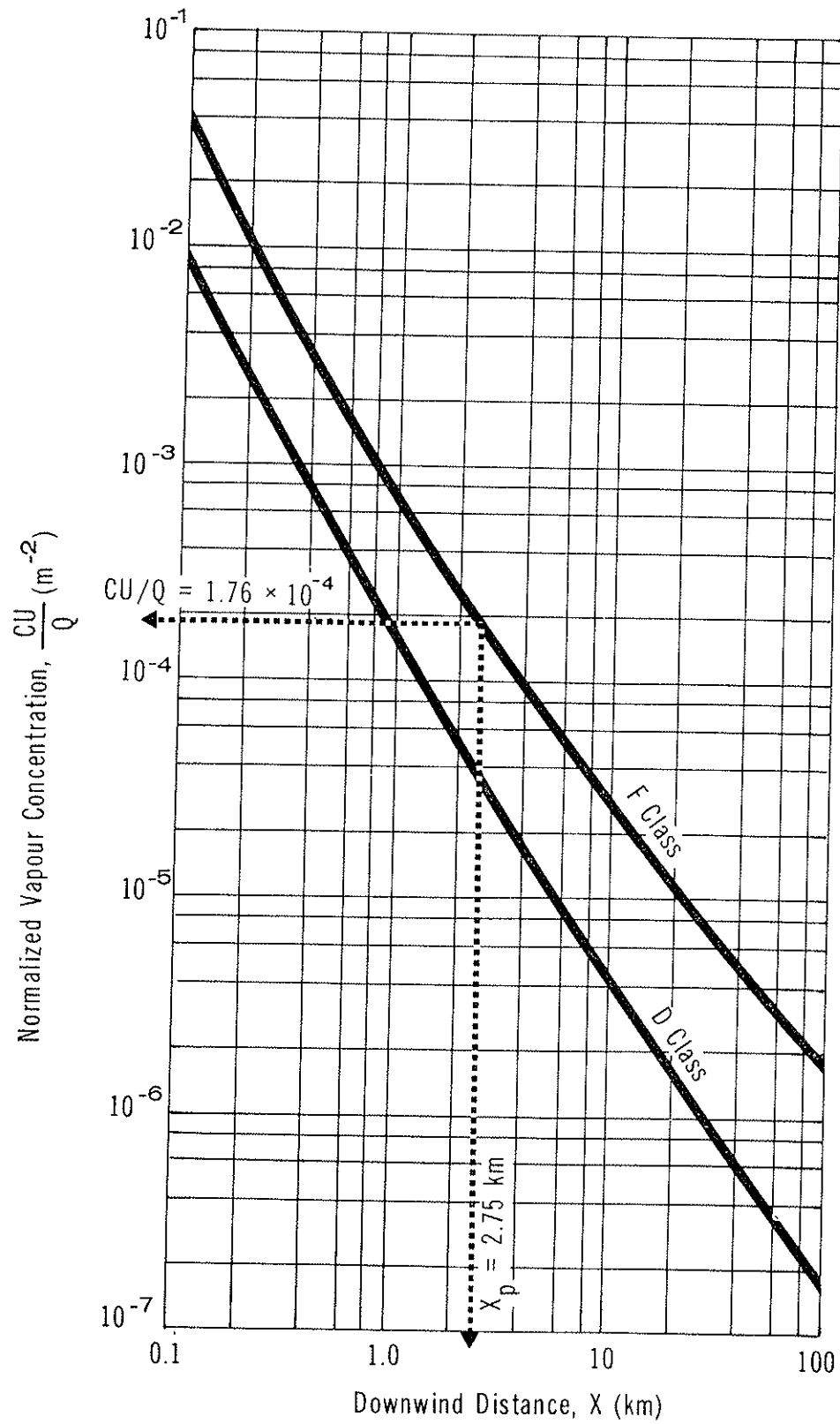
Weather Conditions F	Weather Conditions D
wind speed <11 km/h (3 m/s) and one of the following: - overcast day - night - severe temperature inversion present	most other wind and weather conditions

The following calculations can be performed using Figure 9:

- 1) Given Q, U and the weather condition, the concentration C can be determined for any downwind distance, x. This applies to point source emissions. For area sources, the distance must be adjusted by  $-x_y (=5d)$ .
- 2) Given Q, U, the weather condition and the hazard concentration limit,  $C^*$ , (the lower of the Threshold Limit Value (TLV<sup>®</sup>) or the Lower Flammability (Explosive) Limit (LEL)), the hazard distance downwind can be determined.



ETHYLBENZENE

NORMALIZED VAPOUR CONCENTRATION  
VS DOWNWIND DISTANCE

- 3) Given  $U$ , the weather condition and the hazard concentration limit,  $C^*$ , the maximum vapour release rate ( $Q$ ) which will maintain concentrations below  $C^*$  beyond a specified downwind distance  $x$  can be calculated.

Figure 10 presents an example nomogram derived from equation 9 for a puff release. The curves represent maximum values  $C/Q\tau$  as a function of downwind distance and stability. These are the maximum normalized concentrations which would be observed at any point  $x$  as the puff travels by.

**5.3.4.3 Plume/puff hazard width tabulations.** Table 4 shows maximum ground level vapour plume half-widths  $(W/2)_{\max}$  versus  $Q/U$  for weather conditions (D or F), based on equation (10), for the hazard concentration limit  $C^* = 100 \text{ ppm}$  ( $0.435 \text{ g/m}^3$ ) (the TLV<sup>®</sup> for ethylbenzene).

For a given weather condition, the maximum ethylbenzene vapour plume half-width at  $20^\circ\text{C}$  can be determined for any  $Q/U$ . This "maximum half-width" is used with the maximum hazard distance to delineate the "hazard zone". The typical shape of the hazard zone for a wind from  $270^\circ\text{C}$  (West) is shown in Figure 11 by the dotted line. The area enclosed by the dashed line, defined by  $W/2$  and  $X$ , should be used to define the hazard area. If the wind is fluctuating, as is often the case, and the observation or prediction is given as wind from  $270^\circ \pm 10^\circ$  then the hazard zone would be that defined by the dashed line in Figure 12. The dotted line represents the anticipated hazardous concentration area.

**5.3.4.4 Plume/puff travel time versus travel distance.** Figure 13 presents plume/puff travel time ( $t$ ) versus travel distance ( $x_t$ ) as a function of different wind speeds ( $U$ ). This is simply the graphical representation of the relationship  $x_t = Ut$  for a range of typical winds speeds.

Knowing the time ( $t$ ) since the spill occurred and the wind speed ( $U$ ), Figure 13 shows how far downwind ( $x_t$ ) the vapour plume could have travelled.

**5.3.4.5 Concentration units conversion nomograms.** Figure 14 converts Threshold Limit Value (TLV<sup>®</sup>) concentration from ppm to  $\text{g/m}^3$ . Figure 15 converts Lower Flammability Limit (LFL) concentration from volume percent to  $\text{g/m}^3$ .

### **5.3.5 Summary of Chemical Modelling Considerations.**

**5.3.5.1 Protocol for chemicals modelled as plume releases.** Chemicals modelled as plume releases are those that would form a liquid pool when instantaneously spilled on a

FIGURE 10

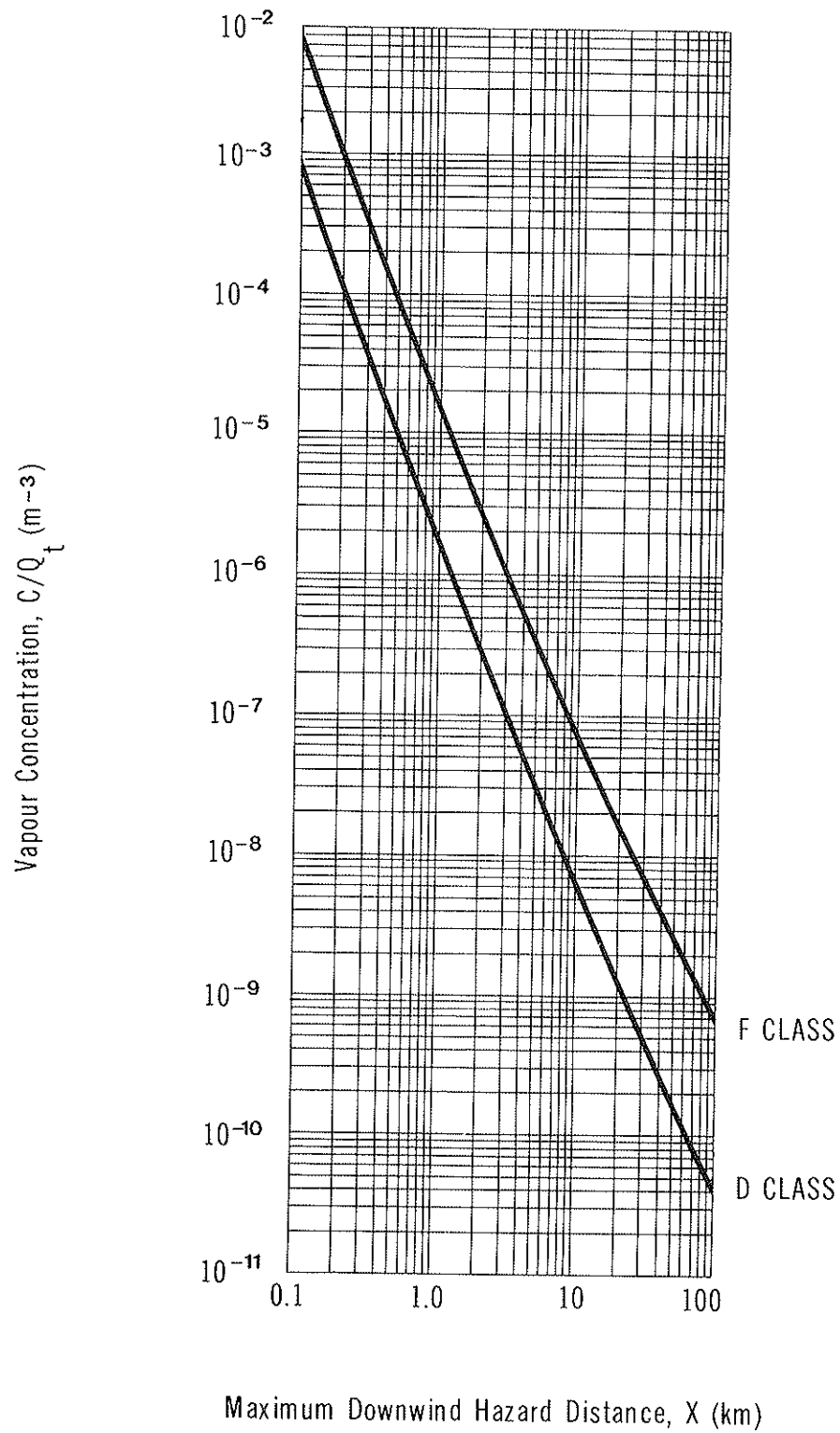
**VAPOUR CONCENTRATION  
VS DOWNWIND DISTANCE**

TABLE 4 MAXIMUM PLUME HAZARD HALF-WIDTHS (for Ethylbenzene at 20°C)

Weather Condition D			Weather Condition F		
Q/U (g/m)	(W/2) <sub>max</sub> (m)		Q/U (g/m)	(W/2) <sub>max</sub> (m)	
30 000 000	3 400	(x < 99.5 km)*	2 500 000	1 385	(x < 99.5 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	
750 000	360	Q/U = 24 760 →	25 000	60	→ (W/2) <sub>max</sub> = 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				
50 000	75				
25 000	50				
10 000	32				
5 000	20				
1 000	10				

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

**Example:** 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  $10 \times \text{TLV}^*$ , or  $4.35$  g/m<sup>3</sup>.

ground or water surface and evaporate over a period of time. The evaporation rate of chemical and the size of the liquid pool are used to determine the vapour emission rate,  $Q$ , for air dispersion calculations. Solid chemicals and liquids with an equilibrium vapour pressure less than the  $10 \times \text{TLV}^*$  are not modelled.

Generally, a consistent set of assumptions was used in determining the vapour hazard zones in the examples. These are:

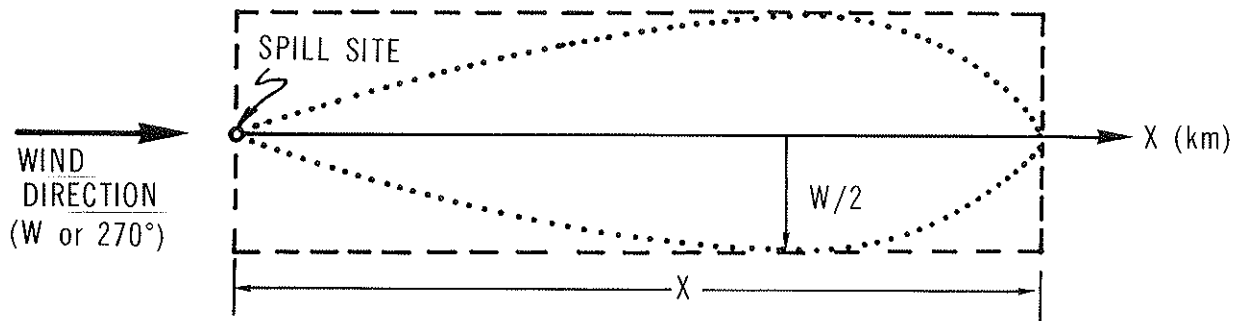


FIGURE 11 HAZARD ZONE MAPPING FOR WIND FROM 270°C

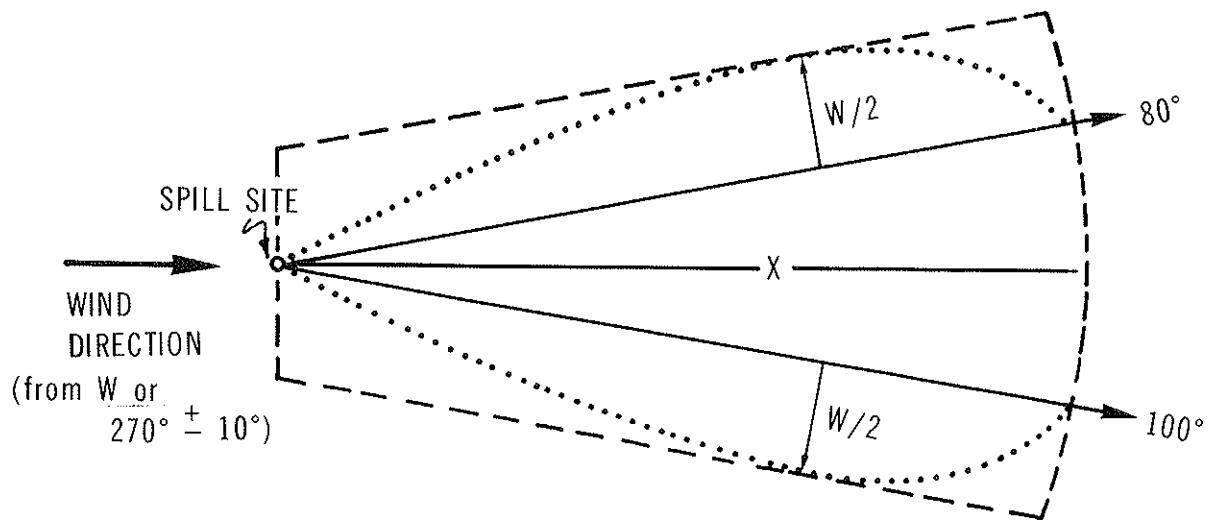
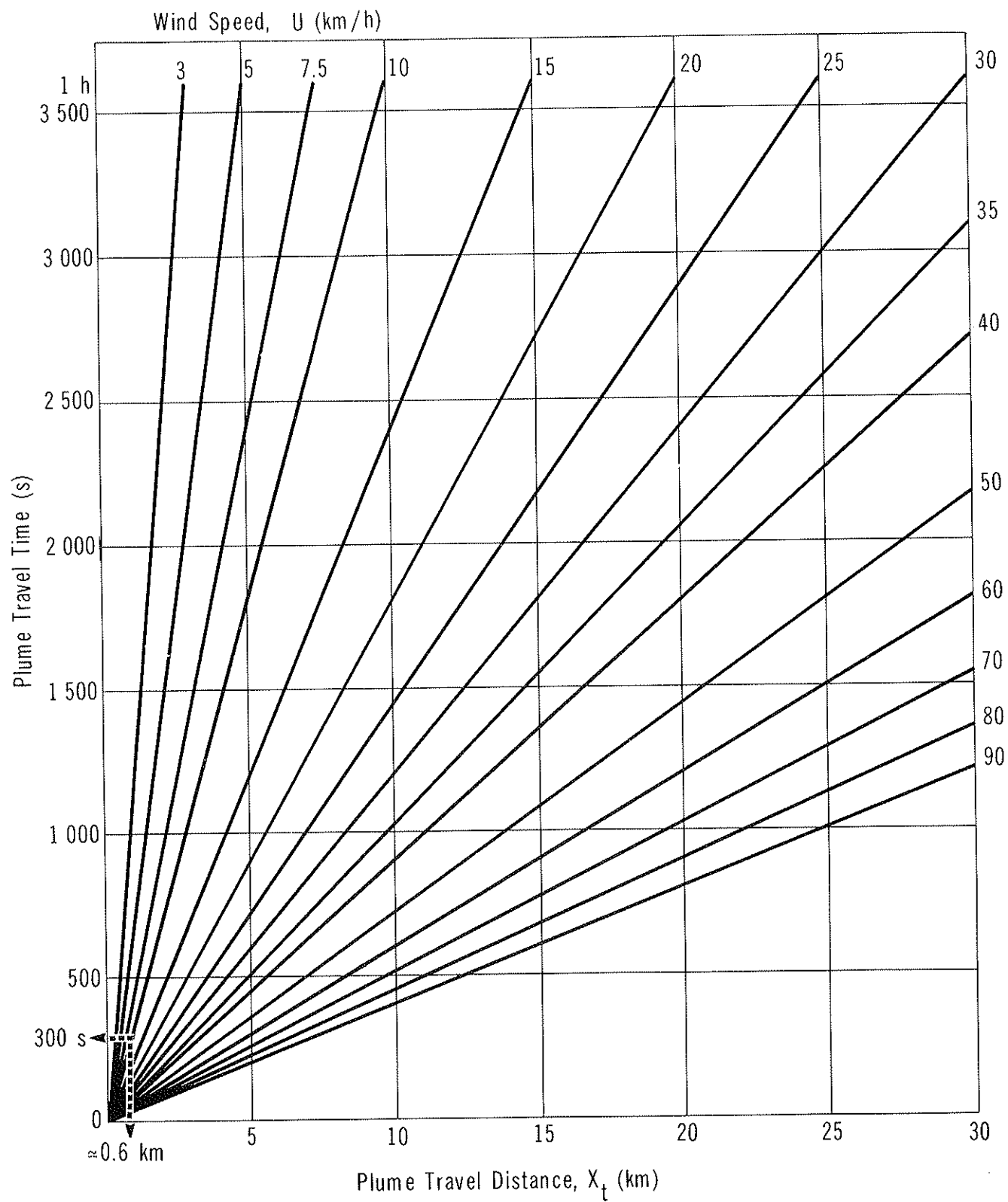


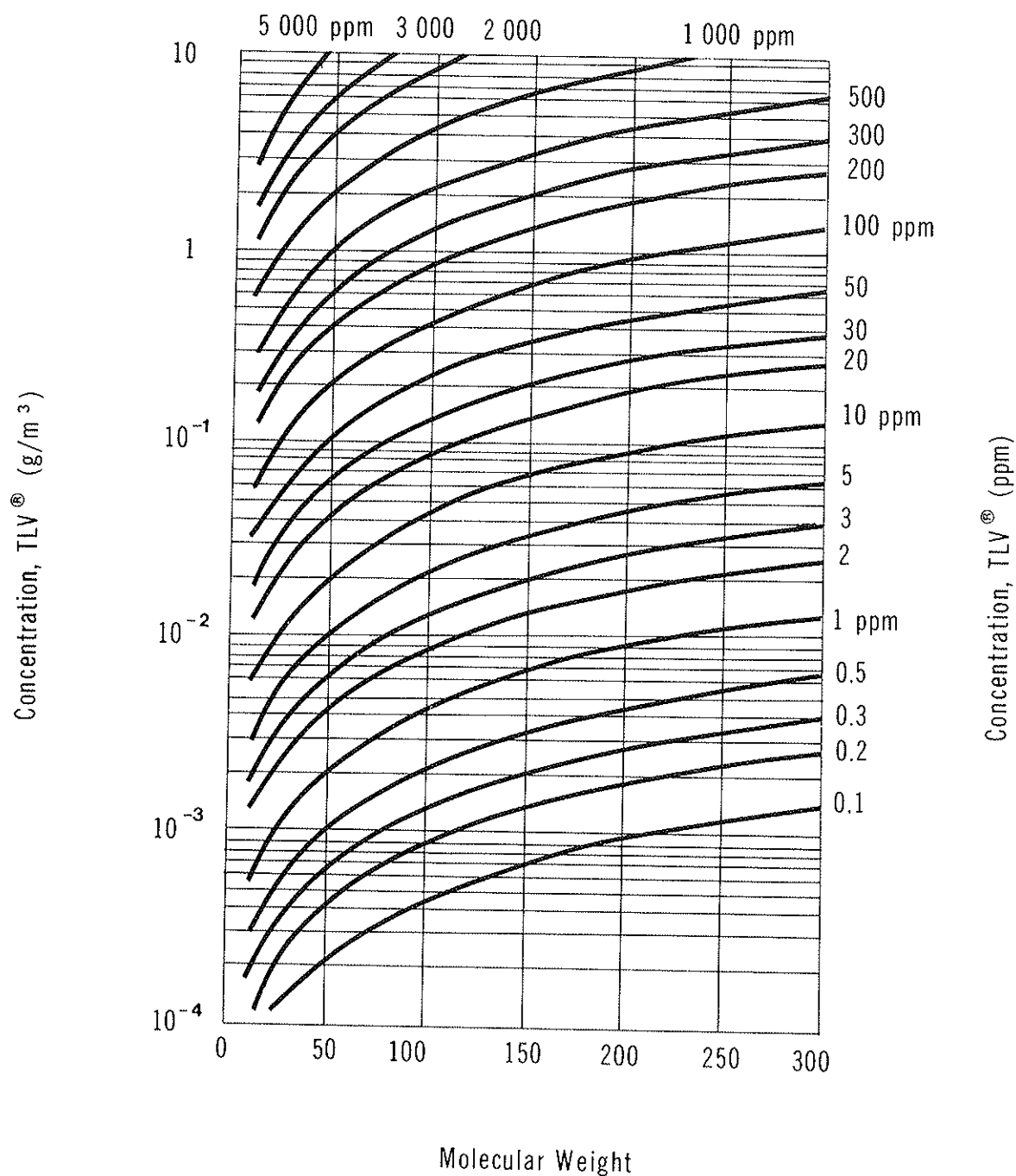
FIGURE 12 HAZARD ZONE MAPPING FOR WIND FROM 270°C ± 10°C

ETHYLBENZENE

**PLUME TRAVEL TIME  
VS TRAVEL DISTANCE**

ETHYLBENZENE

FIGURE 14  
 CONVERSION OF THRESHOLD LIMIT VALUE  
 (TLV®) UNITS (ppm to g/m³)

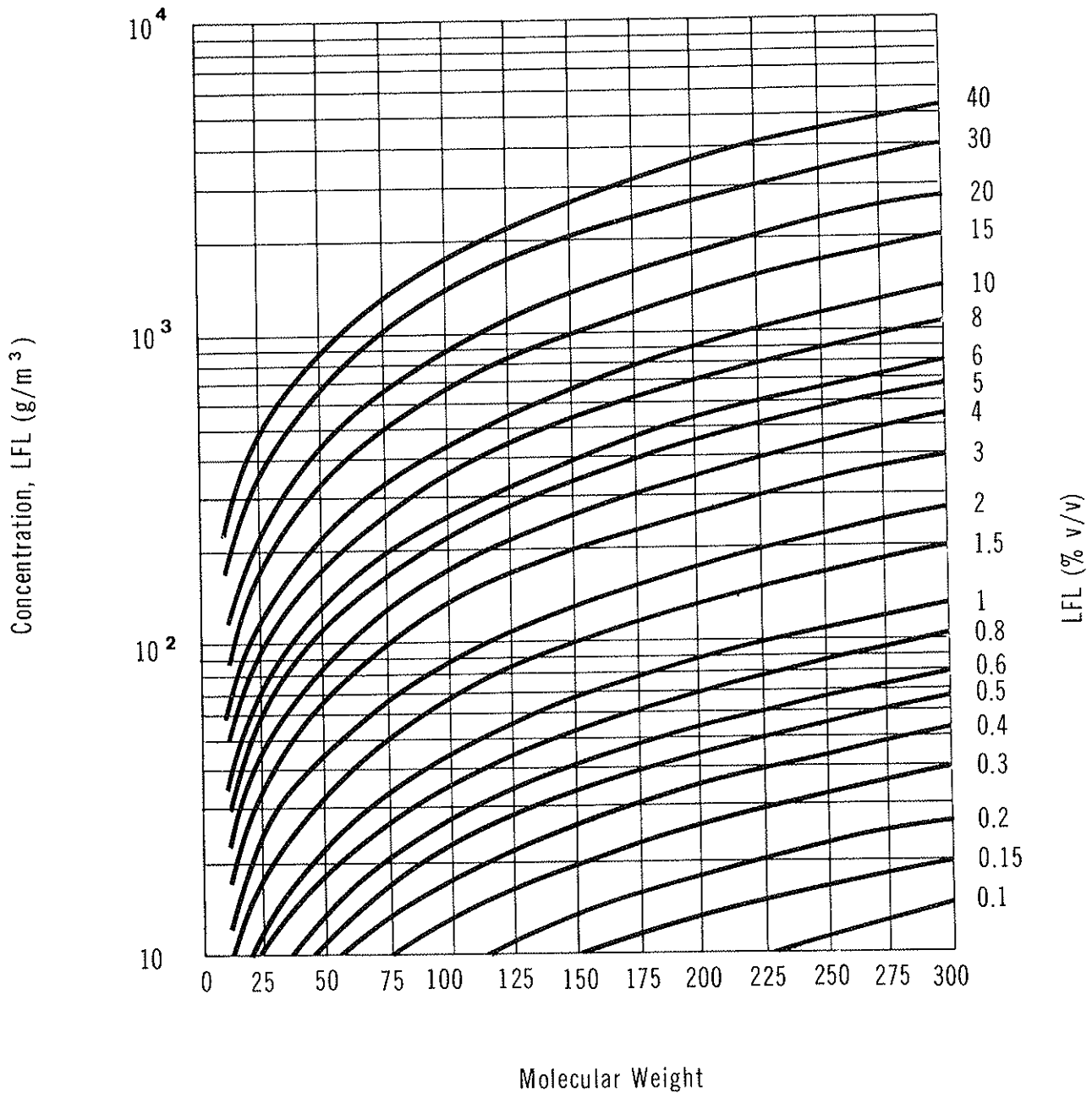


Example: Ethylbenzene, MW = 106. TLV® = 100 ppm,  
 then TLV® in g/m³ = 0.45 g/m³

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

ETHYLBENZENE

# CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m<sup>3</sup>)





- a) an instantaneous 20 tonne liquid spill from a standard 80 000 L rail car;
- b) the spilled material forms a liquid pool with a pool radius determined from the chemical's maximum pool radius using data from CHRIS (1974); and
- c) a hazard concentration limit equal to the lower of the TLV<sup>®</sup> x 10 or the LFL.

For some chemicals modelled as plume releases, these assumptions were not considered appropriate. Explanations are provided in the appropriate manual. They are listed as follows according to the type of exception:

- a) Unusual hazard: red phosphorus (autoignition of solid).
- b) Other spill quantities: red phosphorus (47 000 L).
- c) Maximum liquid pool radius assumed to be equal to that of a chemical treated by CHRIS: toluene, styrene and xylene (ethylbenzene); ethylene dichloride (benzene); propylene oxide (ethyl nitrate).
- d) Maximum liquid pool radius arbitrarily assigned: mercury, tetraethyl lead and sulphuric acid (oleum) (depth of spill set to 2 mm); acetic acid, acetic anhydride, formaldehyde, methanol, morpholine, nitric acid, and butyraldehyde (intermediate value between that of benzene and isoamyl nitrate).
- e) Hazard concentration limit not the lower limit of the TLV<sup>®</sup> x 10 or the LFL or assigned: hydrogen fluoride (IDLH); red phosphorus (phosphoric acid); butyraldehyde (TCLO).

**5.3.5.2 Protocol for chemicals modelled as puff releases.** Chemicals modelled as puff releases are those that would generally produce an instantaneous vapour cloud when spilled on a ground or water surface. The mass of vapour released into the atmosphere is subsequently used in the air dispersion calculations. The assumptions used to determine the vapour hazard zone in the examples are:

- a) an instantaneous 20 tonne liquid spill from a standard 80 000 L rail car;
- b) the spilled chemical forms an instantaneous cloud with 100 percent conversion to vapour;
- c) a hazard concentration limit equal to the lower value of the TLV<sup>®</sup> x 10 or the LFL.

Chemicals modelled as puff releases for which these assumptions were not appropriate are listed below according to the type of exception:

- a) Other Shipping Containers: ethylene, natural gas (varying size storage facilities; but example cases are given for 80 000 L regardless).
- b) Vapour Puff Not 100 Percent: vinyl chloride and ethylene oxide (25 percent).

## 5.4 Behaviour in Water

**5.4.1 Overview and Objectives.** The dispersion of contaminants in water does not in general pose the same magnitude of threat to life and property as does the airborne dispersion of toxic or flammable gases. The long-term environmental effect, however, may be far greater, in terms of both direct toxicity to aquatic life and food chain concentration. Many chemicals are toxic to aquatic biota at very low concentrations; even in large bodies of water it may take a long time for dilution to below-threshold levels to occur. This results in both a toxic environment and a large area of contamination. In addition, even where concentrations are below acute toxicity levels, bioconcentration resulting in increased mortality to species high in the food chain may occur, threatening the viability of some species.

The dispersion behaviour of substances spilled in water depends on several key properties. Models have been developed to describe the spreading of a less-dense, insoluble liquid on a water surface; the sinking and dispersion of a more-dense, insoluble liquid; the mixing and dilution of a soluble material; and the evaporation of a volatile material from a water surface. Worst-case assumptions have been made with the intent of producing a conservative value that will not understate the extent of dispersion under foreseeable circumstances.

**5.4.2 Information Sources.** The nomograms were developed from models presented by Raj (1974). Several other works cited in the text were used in the development of models for specific dispersion conditions. These include, notably:

- "Dynamics of Oil Slicks" (Fannelop and Waldman 1972);
- "A Critical Technical Review of Six Hazard Assessment Models" (Eisenberg 1975);
- "CHRIS Hazard Assessment Handbook" (CHRIS 1974);
- "Chemodynamics, Environmental Movement of Chemicals in Air, Water and Soil" (Thibodeaux 1979);

- "Assessment Models in Support of the Hazard Assessment Handbook" (Raj 1974); and
- "Development of Additional Hazard Assessment Models" (Raj 1977).

### 5.4.3 Derivation of Models and Nomograms.

**5.4.3.1 Spreading of a liquid on water.** The behaviour of a spill of an insoluble, lighter than water chemical has been summarized in four nomograms as shown in the EnviroTIPS manuals. They are:

- spill radius versus time (still water - unconfined) for various sizes of spills, with the maximum spill radius indicated;
- length of channel affected versus equivalent spill radius (still water, confined) for a number of stream widths;
- translation distance versus time for a range of surface water velocities; and
- vectorial addition of surface current and wind.

The spill radius to time relationship was calculated assuming that:

- the chemical is immiscible;
- the water is still (no waves or tide);
- the total mass remains constant;
- the physical properties of the chemical remain constant during the spill;
- the spill occurs instantaneously; and
- the water temperature is 20°C.

The rate of spreading on water is controlled by the balance between forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces). Pool growth has been simplified and described in terms of three controlling interaction stages: gravity-inertia, gravity-viscosity, and viscosity-surface tension.

Each relationship is most predictive of spill radius over a specific elapsed time range, dependent on various spill parameters. Conceptually, the gravity-inertia regime is used for "short" elapsed time, gravity-viscosity for "intermediate", and viscosity-surface tension for "long". The decision mechanisms for selecting the method of radius calculation based on elapsed time are shown in Tables 5 and 6, above the corresponding radius calculation method.

TABLE 5 SPREAD OF A HIGH VISCOSITY LIQUID ON A LOW VISCOSITY LIQUID

Gravity - Inertia	Gravity - Viscosity	Viscosity - Surface Tension
for $t < 0.546 \left[ \frac{V}{G\nu_w} \right]^{1/3}$ ,	for $0.546 \left[ \frac{V}{G\nu_w} \right]^{1/3} < t < 0.375 \frac{\rho_w}{\sigma} \left[ G^2 V^4 \nu_w^2 \right]^{1/6}$ ,	for $t > 0.375 \frac{\rho_w}{\sigma} \left[ G^2 V^4 \frac{2}{\mu_w} \right]^{1/6}$
$r = 1.14 (GV)^{1/4} t^{1/2}$	$r = 0.98 \left[ \frac{G^2 V^4}{\nu_w} \right]^{1/12} t^{1/4}$	$r = 1.6 \left[ \frac{\sigma}{\mu_w \rho_w} \right]^{1/2} t^{3/4}$
$\nu_w$ = kinematic viscosity of water ( $m^2/s$ )		
$\rho_w$ = density of water ( $kg/m^3$ )		
$\mu_w$ = absolute viscosity of water ( $N \cdot s/m^2$ )		
$r$ = pool radius (m)		
$t$ = time since spill (s)		
$V$ = spill volume ( $m^3$ )		
$G = g(1 - \rho_l/\rho_w)$ ( $m/s^2$ )		
$g$ = gravitational constant ( $m/s^2$ )		
$\rho_l$ = density of liquid ( $kg/m^3$ )		
$\sigma$ = interfacial surface tension ( $N/m$ )		

TABLE 6      SPREAD OF A LOW VISCOSITY LIQUID ON A HIGH VISCOSITY LIQUID

Gravity - Inertia	Gravity - Viscosity	Viscosity - Surface Tension
$\text{for } t_1 = 0.4446 \left[ \frac{V}{Gv_l} \right]^{1/3}$		$\text{for } t_2 = 0.1697 \left[ \frac{GV \mu_l^2}{\sigma^2 v_l} \right]$
and $t < t_1$	for $t_1 \leq t \leq t_2$	and $t > t_2$
$r = 1.14 \left[ GV \right]^{1/4} t^{1/2}$	$r = 0.8412 \left[ \frac{GV^3}{v_l} \right]^{1/8} t^{1/8}$	$r = 1.05 \left[ \frac{\sigma V}{\mu_l} \right]^{1/4} t^{1/4}$
$v_l$ = kinematic viscosity of water (m <sup>2</sup> /s) $\mu_l$ = absolute viscosity of liquid (N·s/m <sup>2</sup> ) $\sigma$ = interfacial surface tension (N/m)		

These equations are based on work by Fannelop and Waldman (1972). Those shown in Table 5 are used to predict spill radius versus time for a high viscosity liquid on a low viscosity liquid, while Table 6 predicts spill radii for a low viscosity liquid on a high viscosity liquid. However, a critique of the spreading models (Eisenberg 1975) suggests that the equations for a high viscosity liquid on a low viscosity liquid are also valid for cases where the viscosity of the spilled chemical is at least 0.2 times the viscosity of water. The maximum spill radius shown on the spill radius versus time nomogram in each manual is calculated from the Hazard Assessment Handbook (CHRIS 1974) and is based on the specific gravity of the liquid.

Example: a 20 tonne spill of ethylbenzene has occurred on a large lake. Determine the size of the spill after 20 minutes.

$$\mu_l = 0.00065 \text{ N}\cdot\text{s}/\text{m}^2$$

$$\mu_w = 0.001 \text{ N}\cdot\text{s}/\text{m}^2$$

$$\mu_l > 0.2 \mu_w$$

Therefore the equations describing the spill of a high viscosity liquid on a low viscosity liquid are used to determine the spill radius.

$$\mu_w = 1 \times 10^{-6} \text{ m}^2/\text{s}$$

$$\rho_w = 1000 \text{ kg}/\text{m}^3$$

$$\rho_l = 880 \text{ kg}/\text{m}^3$$

$$\sigma = 0.035 \text{ N}/\text{m}$$

$$V = \text{mass}/\text{density} = 22.7 \text{ m}^3$$

$$G = 1.2 \text{ m}/\text{s}^2$$

For a time of 20 minutes, determine the regime which describes the equation for spreading.

#### Gravity-Inertia

$$t < 0.546 \left[ \frac{V}{G \rho_w} \right]^{1/3}$$

1200s > 145s therefore not gravity-inertia region

#### Viscosity-Surface Tension

$$t > 0.375 \frac{\rho_w}{\sigma} \left[ G^2 V^4 \nu_w^2 \right]^{1/6}$$

1200 s > 913s, therefore, the viscosity-surface tension region

The equation shown in Table 5 gives a spill radius of 61 m, in comparison to the EnviroTIPS manuals graphical value of 60 m.

A simplified relationship was used to determine the length of channel affected, using the spill radius determined from the first nomogram:

$$X = \frac{\pi r^2}{w}$$

where     X = length affected (m)  
             r = equivalent spill radius (m)  
             w = stream width (m)

The distance the spill is translated is determined using:

$$X = 60tU$$

where     X = translation distance (m)  
             t = time (min)  
             U = stream surface velocity (m/s)

The final nomogram was developed to determine the direction and speed of an oil slick moving on an open water body. Following accepted practice, the speed of a slick is assumed to be 3 percent of the measured wind speed plus the vectorial addition of current (CHRIS 1974).

**5.4.3.2 Sinking chemical.** A mathematical model (Thibodeaux 1979) was used to predict the length and width of contamination on the bed of a non-tidal water body. The material represented is assumed to be insoluble, with a density greater than that of water and a boiling point greater than ambient temperature. An example of such a chemical is tetraethyl lead.

The EnviroTIPS manuals present four nomograms to solve for the length and width of the contamination zone. They are:

- fall velocity versus equivalent diameter of puncture for a range of average stream velocities;
- settling time versus fall velocity for a range of stream velocities;
- downstream distance versus settling time for a range of average stream velocities;

- spill width versus equivalent diameter of puncture for a range of stream depths.

The following equation was used to calculate the fall velocity of the smallest droplets resulting from a puncture:

$$d_{\min} = \frac{\sigma K_F \left[ \frac{1000 D \rho_w}{0.1 \mu_w} \right]^{3/5}}{10 \rho_l U_{\text{rel}}^{7/5}}$$

where:  $d_{\min}$  = minimum drop diameter (cm)  
 $K_F$  = experimental constant (0.05468)  
 $D$  = puncture size (m)  
 $\rho_w$  = density of water (g/cm<sup>3</sup>)  
 $\sigma$  = interfacial surface tension (N/m)  
 $\mu_w$  = viscosity of water (g/(cm•s))  
 $\rho_l$  = density of chemical (g/cm<sup>3</sup>)  
 $U_{\text{rel}}$  = relative velocity of chemical (m/s) =  $(U^2 + U_n^2)^{1/2}$   
 $U$  = average stream velocity (m/s)  
 $U_n$  = chemical velocity at puncture (m/s) =  $0.60 (2 gH)^{1/2}$   
 $H$  = height of chemical in tank car (m)

A sensitivity analysis of model input parameters indicated that the length of the zone of contamination was proportional to the height of chemical in the tank car and inversely proportional to the water temperature. A water temperature of 5°C and a chemical height of 2.75 m were used for all calculations. This is consistent with the diameter of the tank car used in the preparation of leak nomograms. Use of these two values will produce conservative results for most spill occurrences.

The equation for determination of minimum droplet size assumes that the chemicals exist in a liquid form. If the chemical is solid, the above calculation is unnecessary and an estimate of minimum particle size is made based on its physical characteristics during transportation.

Droplets are formed as the chemical discharges from the tank and upon entering the water. The terminal fall velocity of the droplets in water is dependent on the flow regime of the falling drop. A dimensionless number which represents a ratio of the gravitational to the viscous forces is used to determine into which regime it may be classified:



$$K = d_{\min} \left[ \frac{g \rho_w \rho_{\text{DIFF}}}{\mu_w^2} \right]^{1/3}$$

where  $K$  = dimensionless number  
 $\rho_{\text{DIFF}}$  = density difference between substance and water ( $\text{g/cm}^3$ )  
 $\mu_w$  = viscosity of water ( $\text{g/(cm}\cdot\text{s)}$ )  
 $g$  = acceleration due to gravity ( $\text{cm/s}^2$ )

If the value of  $K$  is less than 3.3, the terminal fall velocity is calculated by:

$$U_T = \frac{g d_{\min}^2 \rho_{\text{DIFF}}}{18 \mu_w}$$

where  $U_T$  = terminal fall velocity ( $\text{cm/s}$ )

If the value is greater than 43.6

$$U_T = 1.75 \left[ \frac{g d_{\min} \rho_{\text{DIFF}}}{\rho_w} \right]^{1/2}$$

If the value of  $K$  is between 3.3 and 43.6

$$U_T = \frac{0.153 g^{0.71} d_{\min}^{1.14} \rho_{\text{DIFF}}^{0.71}}{\rho_w^{0.29} \mu_w^{0.43}}$$

The relationship between terminal fall velocity, depth, and settling time is:

$$t = \frac{5}{3} \frac{d}{U_T}$$

where  $t$  = settling time (min)  
 $d$  = stream depth (m)

The downstream distance (length of zone of contamination) is related to settling time and average stream velocity:

$$X = 60 U t$$

where  $X$  = downstream distance (m)  
 $U$  = average stream velocity ( $\text{m/s}$ )  
 $t$  = settling time (min)

The width of the contamination zone is a function of the diameter of puncture and the stream depth. The following equations were used to develop the nomogram for spill width (W):

$$F_r = \frac{U_n^2}{g D}$$

where  $F_r$  = Froude number  
 $U_n$  = chemical velocity at puncture (m/s)  
 $D$  = equivalent puncture diameter (m)  
 $g$  = acceleration due to gravity (m/s<sup>2</sup>)

$$W_e = \frac{1000 D U_n^2 \rho_l}{\sigma}$$

where  $W_e$  = Weber number  
 $\rho_l$  = density of chemical (g/cm<sup>3</sup>)  
 $\sigma$  = interfacial surface tension (N/m)

$$R_e = \frac{1000 D U_n \rho_l}{\mu_l}$$

where  $R_e$  = Reynolds number  
 $\mu_l$  = chemical viscosity (kg/(m•s))  
 $\rho_l$  = density of chemical (g/cm<sup>3</sup>)

$$H_e = \frac{d}{D}$$

where  $H_e$  = Height number  
 $d$  = stream depth (m)  
 $D$  = equivalent diameter of puncture (m)

$$A_R = \frac{605 F_r^{0.41} W_e^{0.61}}{R_e^{0.51} H_e^{1.1}}$$

where  $A_R$  = dimensionless area number ( $F_r$ ,  $W_e$ ,  $R_e$  and  $H_e$  are defined above)

therefore 
$$W = \left[ \frac{4 A_R d^2}{\pi} \right]^{1/2}$$

where  $W$  = spill width (m)  
 $d$  = stream depth (m)

Example: Consider a 20 tonne spill of ethylene dichloride in a river. The stream width is 250 m and the depth is 10 m. The stream velocity is 0.5 m/s. Assuming that the equivalent diameter of the puncture is 200 mm, how far downstream will the smallest particle be carried before reaching the streambed and what is the maximum width of the contaminated zone?

$$\begin{aligned}\rho_w &= 1 \text{ g/cm}^3 \\ \mu_w &= 0.0153 \text{ g/(cm}\cdot\text{s)} \\ \sigma &= 0.030 \text{ N/m} \\ \rho_l &= 1.3 \text{ g/cm}^3 \\ \mu_l &= 0.001 \text{ kg/(m}\cdot\text{s)} \\ D &= 0.200 \text{ m} \\ H &= 2.75 \text{ m} \\ U &= 0.5 \text{ m/s}\end{aligned}$$

Summary of calculations:

$$\begin{aligned}U_n &= 4.4 \text{ m/s} \\ U_{rel} &= 4.4 \text{ m/s} \\ d_{min} &= 0.019 \text{ cm} \\ K &= 2.05\end{aligned}$$

Therefore the terminal fall velocity is calculated using:

$$\begin{aligned}U_T &= \frac{980 d_{min}^2 \rho_{DIFF}}{18 \mu_w} \\ &= 0.38 \text{ cm/s} \\ t &= 44 \text{ min}\end{aligned}$$

The smallest particle will be carried 1320 m downstream, compared to 1500 m as determined graphically in the ethylene dichloride manual.

$$\begin{aligned}F_r &= 9.9 \\ W_e &= 167\,787 \\ R_e &= 1\,144\,000 \\ H_e &= 50\end{aligned}$$

$$A_R = 26$$

$$W = 58 \text{ m}$$

The spill width is equal to 58 m, the same as the graphical value.

**5.4.3.3 Mixing and dilution.** Nomograms have been developed to estimate concentrations in non-tidal rivers and to define the hazard zone and the average concentration for still water bodies. The nomograms for non-tidal rivers are:

- time versus distance for a range of average stream velocities;
- hydraulic radius versus channel width for a range of stream depths;
- diffusion coefficient versus hydraulic radius for a range of average stream velocities;
- $\alpha^*$  versus diffusion coefficients for various time intervals;
- $\delta^*$  versus  $\alpha$  for a range of spill sizes;
- maximum concentration versus  $\delta$  for a range of river cross-sectional areas.

The nomograms for still water bodies are:

- volume versus radius for the hazard zone for a range of lake depths;
- average concentrations versus volume for the hazard zone for a range of spill sizes.

Pollutant concentrations for non-tidal rivers are based on equations presented in the "Assessment Models in Support of the Hazard Assessment Handbook" (Raj 1974). The model is applicable to neutrally buoyant liquids that are miscible with water. Pollutant concentrations are considerably more difficult to determine for chemicals much denser or lighter than water. In order to consider the effects of buoyancy analytically, it is necessary to solve the system of partial differential equations comprised of the continuity, momentum and diffusion equations. The model assumed an idealized rectangular channel and a uniform concentration of pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream that mixing and dilution have distributed the pollutant evenly across the channel. This is termed a 'far field' approximation. The model assumes an instantaneous spill and is applicable to rivers where the ratio of width to depth is less than 100.

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\*  $\alpha$  and  $\delta$  are intermediate terms with no physical significance; they are used to facilitate calculation of downstream concentration.

The relationship used to derive the nomogram of time versus distance for a range of stream velocities is:

$$t = \frac{X}{60 U}$$

where  $t$  = time (min)  
 $X$  = distance (m)  
 $U$  = average stream velocity (m/s)

The hydraulic radius of a rectangular channel is defined by:

$$r = (W \times d)/(W + 2d)$$

where  $r$  = hydraulic radius (m)  
 $W$  = width of river (m)  
 $d$  = depth of river (m)

The diffusion coefficient used to determine the pollutant concentration is:

$$E = 225 U^* r$$

where  $E$  = diffusion coefficient ( $m^2/s$ )  
 $r$  = hydraulic radius (m)  
 $U^*$  = shear velocity (m/s)

The shear velocity is defined as:

$$U^* = 3.115 n \frac{U}{r^{1/6}}$$

where  $n$  = Roughness coefficient ( $m^{1/6}$ )  
 $U$  = average stream velocity (m/s)  
 $r$  = hydraulic radius (m)

The "Roughness coefficient" describes the resisting force of the watercourse to flow. Its value may range from a minimum of 0.020 to a maximum of 0.050. All watercourses would have different values. An average of 0.030 has been chosen for this study.

The maximum far field pollutant concentration is calculated by:

$$C = \frac{\text{mass}}{A \sqrt{4\pi Et}}$$

where     C     = concentration (kg/m<sup>3</sup>)  
           A     = cross-sectional area of flow (m<sup>2</sup>)  
           E     = diffusion coefficient (m<sup>2</sup>/s)  
           mass = mass of spill (kg)  
           t     = time (s)

Three nomograms are required to solve the equation for pollutant concentration as a function of A, E, mass and t. The first nomogram solves for:

$$\alpha = \sqrt{240 \pi E t}$$

where      $\alpha$  = alpha, intermediate term (m)  
           E = diffusion coefficient (m<sup>2</sup>/s)  
           t = time (min)

The second nomogram solves for:

$$\Delta = \frac{\text{mass}}{\alpha} \times 1000$$

where      $\Delta$      = delta, intermediate term (kg/m)  
           mass = mass of spill (tonnes)  
            $\alpha$      = alpha (m)

The third nomogram solves for the concentration

$$C = \frac{\Delta/A}{\Delta/A + \rho_w} \times 10^6$$

where     C = concentration (ppm)  
            $\Delta$  = delta (kg/m)  
           A = cross-sectional area (m<sup>2</sup>)  
            $\rho_w$  = density of water (kg/m<sup>3</sup>)

Example: A 20 tonne spill of 50 percent acetic acid solution has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream:

mass =     10 tonnes  
       t     =     83.3 min

$$\begin{aligned}
 r &= 4.2 \text{ m} \\
 U^* &= 0.074 \\
 E &= 69.9 \text{ m}^2/\text{s} \\
 \alpha &= 2095 \text{ m} \\
 \Delta &= 4.8 \text{ kg/m} \\
 C &= 19.2 \text{ ppm}
 \end{aligned}$$

The concentration of 19.2 ppm agrees well with the graphical solution value of 20 ppm as presented in the acetic acid manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

The nomogram defining volume as a function of radius and depth was calculated by assuming a cylindrical shape. The radius represents the distance from the spill to the point of interest.

$$V = \pi r^2 d$$

where  $V$  = volume ( $\text{m}^3$ )  
 $r$  = radius (m)  
 $d$  = depth (m)

The average concentration is defined as:

$$C = \frac{\text{mass}}{1000 \text{ mass} + (\rho_w \times V)} \times 10^9$$

where  $C$  = average concentration (ppm)  
 $\text{mass}$  = spill size (tonnes)  
 $\rho_w$  = density of water ( $\text{kg/m}^3$ )  
 $V$  = volume of cylinder ( $\text{m}^3$ )

**5.4.3.4 Volatile chemicals.** The nomograms for the spill of volatile chemicals on water presented in the EnviroTIPS manuals were based on values abstracted from the "Hazard Assessment Handbook" (CHRIS 1974). The values for the 10 chemicals presented are shown in Table 7, as abstracted from sections D, K and V. The nomograms were prepared after converting the values from Imperial to metric units.

Three models, described in the "Assessment Models in Support of the Hazard Assessment Handbook" (Raj 1974), were used to estimate the pool radii as a function of

TABLE 7 MAXIMUM POOL RADIUS AND TIME FOR COMPLETE EVAPORATION, METRES (minutes)

Chemical Name	Spill Size (Tonnes)															
	up to 0.1	0.1 to 0.5	0.5 to 1	1 to 5	5 to 10	10 to 30	30 to 60	60 to 125	125 to 250	250 to 500	500 to 1000	1000 to 2000	2000 to 4000	4000 to 8000	>8000	
Ammonia, Anhydrous	6 (1.2)	9 (1.6)	12 (1.9)	20 (2.6)	26 (3.2)	36 (4.1)	45 (4.9)	60 (5.8)	75 (6.8)	93 (8.0)	117 (9.4)	150 (11)	186 (13)	237 (15)	279 (17)	
Hydrogen Fluoride	6 (31)	8 (40)	11 (49)	17 (67)	23 (82)	30 (100)	42 (120)	51 (140)	66 (170)	84 (200)	105 (230)	132 (270)	165 (310)	207 (360)	246 (410)	
Benzene	14 (3)	20 (4)	26 (7)	42 (13)	54 (17)	72 (25)	90 (34)	180 (44)	138 (54)	180 (65)	240 (79)	315 (94)	420 (117)	555 (145)	675 (165)	
Ethylene	5 (0.3)	6 (0.4)	9 (0.5)	15 (0.7)	21 (1.0)	30 (1.2)	42 (1.4)	54 (1.7)	72 (2.1)	96 (2.4)	123 (2.9)	162 (3.4)	210 (4.1)	273 (4.9)	330 (5.5)	
Hydrogen Sulphide	3 (0.8)	5 (1.0)	8 (1.3)	12 (1.8)	18 (2.2)	26 (2.8)	36 (3.4)	45 (4.0)	60 (4.8)	78 (5.6)	102 (6.7)	135 (7.8)	177 (9.3)	231 (11)	279 (13)	
Propylene	5 (0.5)	6 (0.6)	9 (0.7)	17 (1.0)	23 (1.3)	33 (1.6)	48 (2.0)	60 (2.3)	78 (2.8)	102 (3.3)	135 (3.9)	177 (4.6)	228 (5.5)	300 (6.5)	360 (7.4)	
Vinyl Chloride	3 (1.3)	5 (1.8)	6 (2.2)	12 (3.0)	17 (3.7)	24 (4.7)	33 (5.7)	45 (6.7)	57 (8.0)	75 (9.4)	99 (11)	132 (13)	171 (16)	222 (19)	273 (21)	
Ethylene Oxide	6 (3.1)	8 (3.9)	11 (4.8)	18 (6.6)	24 (8.1)	33 (10)	42 (12)	54 (14)	69 (17)	87 (20)	108 (23)	138 (27)	174 (31)	219 (37)	258 (41)	
Cyclohexane	14 (2)	21 (4)	29 (6)	45 (11)	57 (15)	75 (21)	96 (29)	114 (37)	150 (46)	198 (54)	264 (67)	345 (81)	465 (99)	615 (122)	750 (141)	
Naphtha-VM&P	9 (2)	12 (3)	18 (4)	27 (7)	33 (8)	48 (10)	69 (12)	90 (15)	120 (18)	159 (22)	210 (27)	273 (30)	360 (37)	480 (47)	600 (54)	

( ) time for complete evaporation (minutes), derived from Hazard Assessment Handbook (CHRIS 1974)



time after the spill. The model for each substance is chosen according to which of the following classes the substance's physical characteristics match:

- the substance is insoluble or slightly soluble in water, floats on water, and has a boiling point above ambient temperature - examples are benzene, cyclohexane and naphtha;
- the substance is insoluble or slightly soluble in water, floats and has a boiling point below ambient temperature - examples are ethylene, hydrogen sulphide, propylene and vinyl chloride; and
- the substance is soluble in water and has a boiling point below ambient temperature - examples are ammonia, hydrogen fluoride and ethylene oxide.

The time history of the spill size was not calculated because of the short times involved for complete evaporation. A maximum water temperature of 20°C is assumed in the spill modelling as it represents a reasonable maximum temperature of surface water bodies. It should be noted that the higher the water temperature, the smaller the maximum spill size and the shorter the time for complete evaporation. The principal purpose of the nomograms is to describe the maximum spill radius and evaporation times which are to be used for air dispersion modelling. Although the nomograms give maximum spill radii which are not conservative in nature, they do yield times of evaporation which are conservative. A limited amount of modelling was performed to check the values presented in the Hazard Assessment Handbook (CHRIS 1974).

## **5.5 Subsurface Behaviour: Penetration into Soil**

**5.5.1 Overview and Objectives.** In spill circumstances, penetration of the spilled material into the soil and toward the groundwater table can be a major concern. To estimate the magnitude of such potential problems, this work provides graphical representations of penetration depth versus time for various concentrations of spilled substances at different temperatures and in different types of soils.

It must be recognized that, at an actual spill site, only very limited data may be expected regarding soil and groundwater conditions. Consequently, nomograms for estimating soil penetration have been established using simplified assumptions. These require only very basic site data and for the most part provide worst-case estimates of penetration. If more precise estimates of penetration are required than those presented,

both more detailed site investigation and more complex solutions to the equations for contaminant transport would be needed.

Both gravitational and physicochemical forces influence the penetration of liquids into soil. While the gravitational effect moves a liquid downward through the pore and fissure system of a soil, capillary forces caused by interaction between the liquid and the soil can also influence liquid movement. For example, in the case of a water spill on dry soil, capillary action will draw the liquid into the soil.

The extent of liquid penetration produced by these forces depends mainly on the resistance provided by the various soil types and their geometry, the moisture regime within the soil, the penetrating liquid properties, the vegetation, and the temperature. For any spill, the prediction of liquid penetration requires the solution of a complex set of equations specific for the conditions of the spill.

**5.5.2 Information Sources.** The equations required to describe the penetration of fluid into soil include the Darcy Equation, continuity equations, and equations of state relating flow properties to various soil and liquid conditions. The Darcy equation can be written as follows (Freeze and Cherry 1979):

$$v = -K \left[ \frac{dh}{dl} \right] \quad (1)$$

where  $v$  = specific discharge or Darcy velocity (m/s)

$K$  = hydraulic conductivity (m/s)

$l$  = the direction of flow (m)

$h$  = hydraulic head (m)

$$= Z + \Psi \quad (2)$$

$Z$  = elevation head, m

$\Psi$  = pressure head

The  $\frac{dh}{dl}$  term is the hydraulic gradient and combines the gravitational and physicochemical forces which drive the flow. The hydraulic conductivity,  $K$ , embodies the resistance of the soil to the passage of the fluid. It is influenced by the liquid content of the soil ( $\theta$ ) such that:

$$K = F(\theta) \quad (3)$$

$K_0$  =  $K$  at soil pore saturation with liquid

The influence of liquid and soil properties is given by:

$$K_0 = (\rho g)k/m \quad (4)$$

where  $\rho$  = liquid density ( $\text{kg/m}^3$ )  
 $\mu$  = absolute liquid viscosity ( $\text{Pa}\cdot\text{s}$ )  
 $k$  = intrinsic permeability of the soil ( $\text{m}^2$ )  
 $g$  = acceleration due to gravity ( $9.81 \text{ m/s}^2$ )

The continuity equations are algebraic expressions which account for the conservation of fluid during transport and which include fluid retention in the soil, evaporation and transportation. The equations of state are mixtures of algebraic and tabular expressions.

The simultaneous solution of these equations is generally in one dimension, (downward) although lateral movement can occur because of capillary forces and variable soil conditions. The more complex solutions are achieved with approximate numerical methods (as opposed to analytical methods) and frequently require computerization.

**5.5.3 Development and Presentation of Data.** To use these equations accurately to predict contaminant penetration at a specific spill site would require extensive documentation of the site's soil stratigraphy, properties, and soil moisture profiles. In many spill situations, it is unlikely that such data would be collected prior to the need for an initial response to the threat of soil and groundwater contamination. As a consequence, a simplified method to predict penetration has been developed for use in this work. Because of the simplifications involved, the penetration predictions are to be used only as approximate estimates. However, where possible, attempts have been made to produce "worst case" predictions.

Liquid penetration is considered as saturated piston flow. Physicochemical effects are neglected so that flow is driven only by gravity. Prior to the penetration of the spilled contaminant, the soil is considered to be at field capacity. The field capacity is the greatest amount of water that a soil can hold in its pore spaces after excess water has drained away. As the saturated piston flow occurs, the hydraulic conductivity equals the saturated hydraulic conductivity ( $K = K_0$ ). Consequently, penetration nomograms are based on the linear relationship:

$$u = K_0, \quad \text{and} \quad (5)$$

$$B = ut_B \quad (6)$$

where  $B$  = depth of penetration (m)  
 $t_B$  = time of penetration (s)  
 $u$  = flow rate

Three soils, coarse sand, silty sand and clay till, have been chosen to provide a range of possible site conditions. Relevant properties are given as:

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

Penetration nomograms have been prepared for each soil assuming uniform conditions throughout the depth. From the point of view of soil penetration, the substances have been categorized as:

- liquid under pressure, immiscible (LUPI)
- liquid under pressure, miscible (LUP)
- immiscible liquids, "sinkers" (LIS)
- immiscible liquids, "floaters" (LIF)
- miscible liquids (LM)
- soluble solids (SS)
- insoluble solids (SI)

The following characteristics were used in the development of the penetration nomograms.

**5.5.3.1 Liquids under pressure.** When spilled, it is expected that liquids under pressure will evaporate rapidly. In the worst case, however, some may penetrate the soil; therefore, penetration nomograms have been prepared. Evaporation rates presented elsewhere in the manuals can be used to estimate the amount of liquid remaining for various penetration times. The same approach can be applied to the highly volatile liquids.

**5.5.3.2 Immiscible liquids.** Spilled immiscible liquids have been treated in a multi-phase flow mode. Soil water has been considered to be constant at field capacity. As the immiscible liquid moves down according to equations (4) and (5), a residual amount of the liquid ( $S_0$ ,  $\text{m}^3/\text{m}^3$ ) remains within the soil pores. The values of  $S_0$  were chosen based on

oil penetration into soil (Blokke 1971). Downward penetration continues until the amount of liquid spilled per unit of soil surface area ( $B_0$ ) equals the amount retained in the soil pores ( $S_0$ ).

The penetration depth is calculated from equation (6):

$$B = B_0/nS_0 \quad (7)$$

If the groundwater table is reached, the LIF contaminants will form a layer or "pancake" within the capillary fringe of the groundwater table. The LISs will continue to move down into the saturated groundwater zone.

**5.5.3.3 Miscible liquids.** Penetration nomograms were developed for the undiluted miscible liquids as well as for various dilutions. Highly diluted liquids were assumed to have the same penetration rates as water.

**5.5.3.4 Solids.** Spilled insoluble solids were not considered to penetrate the soil at all. For spilled soluble solids, a worst case situation was used in which precipitation was assumed to occur prior to cleanup. This would result in the production of solutions of the contaminant available for penetration into the soil.

Penetration nomograms were prepared for concentrated (10 to 30 percent by weight) and dilute (water) solutions of the contaminant. As a worst case condition, interactions between soils and contaminants, such as adsorption and precipitation, were not included in the analysis.

**5.5.3.5 Report format.** For each contaminant, the specific properties  $\rho$ ,  $\mu$ , and where applicable  $S_0$ , have been tabulated at 20°C and 4°C. Nomograms showing depth of penetration versus elapsed time for each soil type and each temperature are presented, with examples outlining their use.

## **6 ENVIRONMENTAL DATA**

### **6.1 Overview and Objectives**

This section of the EnviroTIPS manual series presents information on the nonhuman toxicity of each substance. The toxicity to aquatic life is strongly emphasized. This does not represent a bias toward aquatic toxicity concerns. Dispersion of toxic materials into water often results in contamination that is much more enduring than dispersion in air; therefore, dilution and transport away from the site are much less effective at reducing the effect. In addition, bioconcentration from water has been much more of an environmental problem than that from land sources. Where land contamination is considered to represent a major threat, it too is emphasized.

### **6.2 Information Sources**

Because the aquatic threat is widely recognized, both environmental and drinking water standards for many materials can be found. These standards are included as representative of degree-of-hazard levels for substances in water. Fewer jurisdictions have regulated airborne pollutant levels; however, in cases where these limits exist, they have been included. Airborne limits are often directed toward neighbouring human health considerations, in contrast to environmental water requirements.

The Registry of Toxic Effects of Chemical Substances (RTECS) includes a rating for aquatic toxicity of chemicals. These values have been shown in the manuals as indicators of the order of magnitude of the toxicity of each substance. The RTECS value given is only to within an order of magnitude, i.e., 10 to 100 ppm for styrene. The parameter is the 96-hour median lethal toxicity threshold ( $TL_{m\ 96}$ ) or alternatively the 96-hour median tolerance limit. This is not to be considered as a safe range for aquatic life, but as a scale for comparing the relative toxicities of different chemicals.

Data on toxicity to aquatic life have been collected both from fish (etc.) kills resulting from spills and from laboratory testing results. Also, data on environmental effects on airborne or soil contaminants have been included where possible. Primary sources for these include a wide range of environmental publications. OHM-TADS has provided considerable secondary source information, as have EPA and state Water Quality Criteria publications.

### 6.3 Selection and Presentation of Data

This section summarizes the literature on the environmental effects of each substance. In some cases, massive bodies of information are available; in these instances, the most recent or applicable material has been used. Where a substance has not been the subject of much research, the information available tends to be more limited in scope, reflecting the special interest of a researcher. Where no research has been documented on a specific substance, properties for related materials are discussed where relevant.

Data derived from actual spill incidents (observed fish kills) and laboratory toxicity tests generally reflect widely different conditions as far as water quality, aeration, temperature, pH, etc., are concerned. Consequently, the data reflect these variations in exposure conditions. Where possible, representative data from extreme as well as from normal conditions are quoted. Where conditions have been documented in a report, these data are preferred. Because documentation of conditions may have been more sparse in older work, the most recent work available has been preferred.

### 6.4 Glossary

The terminology used in this section is fairly consistent with that found in the literature. For terms whose definitions vary, definitions used here have been presented. In addition, a glossary of species names referred to through the EnviroTIPS series has been prepared, ordered alphabetically both by common name and scientific name.

#### Glossary of Terms

Bioconcentration Factor	the ratio of the concentration of a substance in an organism to the concentration in the ambient water
BOD	"biochemical oxygen demand" - a measure of the quantity of oxygen utilized in the biochemical oxidation of organic matter in a specified time and at a specific temperature; it is not related to the oxygen requirements in chemical combustion, being determined entirely by the availability of the material as a biological food and by the amount of oxygen utilized by the microorganisms during oxidation; BOD <sub>5</sub> is the BOD in 5 days; given here in kg of oxygen per kg of substance
COD	chemical oxygen demand - the quantity of oxygen required to consume the substance as measured by treatment with oxidizing agents under specific conditions

LC <sub>50</sub>	lethal concentration - the concentration of a test material that causes death to 50 percent of the test population in a specified test period; the number referring to the percentage of the population
LD <sub>50</sub>	lethal dose - the amount of test material that causes death to 50 percent of the test population in a specified time period; the number referring to the percentage of the population
LC <sub>100</sub> , LC <sub>0</sub> , LD <sub>100</sub> , LD <sub>0</sub>	- see above
Organoleptic	affecting human senses, particularly taste and smell
Th.OD	theoretical oxygen demand - the amount of oxygen that would be required to oxidize the substance to its theoretical ultimate oxidation products
TL <sub>m</sub> 96	96-hour median lethal threshold concentration, or the concentration causing death in one half the test specimens in a 96-hour exposure

### Glossary of Test Species Names

<u>Common Name</u>	<u>Scientific Name</u>
Abalone	<i>Haliotis</i> sp.
Algae	<i>Scenedesmus obliquus</i>
American eel	<i>Anguilla rostrata</i>
American hardshell clam	<i>Venus mercenaria</i>
American oyster	<i>Crassostrea virginica</i>
American shad	<i>Alosa sapidissima</i>
Anchovy	<i>Stolephorus purpureus</i>
Atlantic kelp	<i>Laminaria digitata</i>
Atlantic salmon	<i>Salmo salar</i>
Atlantic silverside	<i>Menidia menidia</i>
Bacteria	<i>E. coli</i> , <i>E. typhosa</i> , <i>Pseudomonas putida</i> , <i>P. fluorescens</i>
Barnacles	<i>Elminius modestus</i>
Bleak	<i>Alburnus alburnus</i>
Bluefish	<i>Pomatomus saltatrix</i>
Blue crab	<i>Callinectes sapidus</i>
Bluegill	<i>Lepomis macrochirus</i>
Blue-green algae	<i>Anabaena</i> sp., <i>Microcystis aeruginosa</i>
Bluntnose minnow	<i>Pimephales notatus</i>
Bream	<i>Abramis brama</i>
Brine shrimp	<i>Artemia salina</i>
Brook trout	<i>Salvelinus fontinalis</i> , <i>Salmo trutta</i>
Brown mussel	<i>Mytilus edulis</i>
Brown shrimp	<i>Crangon crangon</i>
Bullfrog	<i>Rana catesbiana</i>
Bush bean	<i>Phaseolus vulgaris</i>



Caddisflies  
 Carp  
 Catfish  
 Channel catfish  
 Chinook salmon  
 Chub  
 Cockle  
 Cod  
 Coho salmon  
 Common toad  
 Crab  
 Creek chub  
 Croaker  
 Cutthroat trout

Dace  
 Daddy longlegs  
 Damselfly  
 Dungeness crab  
 Daphnid  
 Diatom

Diving beetle  
 Dragonflies

Eel  
 Emerald shiner  
 English sole

Fathead minnow  
 Flounder  
 Frog  
 Fruitfly  
 Fungus

Garden cress  
 Golden shiners  
 Goldfish  
 Grass shrimp  
 Green algae

Green sunfish  
 Guppy

Hard clam  
 Herring  
 Honey bee  
 Housefly

*Stenonema* sp.  
*Cyprinus carpio*  
*Ictalurus nebulosus*  
*Ictalurus punctatus*  
*Oncorhynchus tshawytscha*  
*Squalius cephalus*  
*Cerastoderma edule*  
*Gadus morrhua*  
*Oncorhynchus kisutch*  
*Bufo bufo*  
*Cancer franciscorum*  
*Semolitus atromaculatus*  
*Micropogon undulatus*  
*Salmo clarki*

*Leuciscus leuciscus*  
 Arachnida  
 Zygoptera  
*Cancer magister*  
*Simocephalus* sp.  
*Phaeodactylum tricornutum*, *Skeletonema costatum*  
 Hemiptera  
 Odonata

*Anguilla anguilla*, *Anguilla vulgaris*  
*Notropis atherinoides*  
*Parophrys vetulus*

*Pimephales promelas*  
 Hippoglossoidae  
 Salientia  
*Drosophila melanogaster*  
*Aspergillus niger*

*Lepidium sativum*  
*Notemigonus crysoleucas*  
*Carassius auratus*  
*Hippolyte zostericola*, *Palaemonetes pugio*  
*A. falcatus*, *Chlorella pyranoidosa*, *Chlorella vulgaris*, *Cladophora*, *Scenedesmus quadricauda*  
*Lepomis cyanellus*  
*Lebistes reticulatus*

*Mercenaria mercenaria*  
*Clupea harengus*  
*Apis mellifera*  
*Musca domestica*

<u>Common Name</u>	<u>Scientific Name</u>
Japanese eel	<i>Anguilla japonica</i>
Japanese medaka	<i>Oryzias latipes</i>
Killifish	<i>Fundulus diaphanus</i>
King salmon	<i>Oncorhynchus tshawytscha</i>
Kelp	<i>Macrocystis pyrifera</i>
Lake trout	<i>Salvelinus namaycush</i>
Largemouth bass	<i>Micropterus salmoides</i>
Leopard frog	<i>Rana pipiens</i>
Leech	<i>Hirundinea</i>
Little neck clam	<i>Protothaca staminea</i>
Lobster, Japanese	<i>Panulirus japonicus</i>
Marine diatom	<i>Nitzschia linearis</i>
Marine mussel	<i>Mytilus edulis</i>
Marine pin perch	<i>Lagodon rhomboides</i>
Marsh clam	<i>Pelecypoda</i>
Mayfly	<i>Ephemerella subvaria</i>
Midge	<i>Chironomus plumosus</i>
Minnow	<i>Phoxinus phoxinus</i>
Mosquito fish	<i>Gambusia affinis</i>
Mullet	<i>Mugil cephalus</i>
Mummichog	<i>Fundulus heteroclitus</i>
Mussel	<i>Mytilus edulis</i>
Mysid shrimp	<i>Mysidaceae</i>
Northern anchovy	<i>Engraulis mordax</i>
Northern lobster	<i>Homarus americanus</i>
Northern pike	<i>Esox lucius</i>
Ocean pout	<i>Macrozoarces americanus</i>
Oysters	<i>Ostreidae</i>
Pacific herring	<i>Clupea pallasii</i>
Pacific oyster	<i>Crassostrea gigas</i>
Penacid prawn	<i>Metapenaeus monoceros</i>
Perch	<i>Perca fluviatilis</i>
Periwinkle	<i>Littorina sp.</i>
Phantom midge	<i>Ceratopogonidae</i>
Pickerel	<i>Stizostedion vitreum</i>
Pike	<i>Esox sp.</i>
Pilot whale	<i>Globicephala sp.</i>
Pinfish	<i>Lagodon rhomboides</i>
Plaice	<i>Pleuronectes platessa</i>
Planarian worm	<i>Polycelis nigra</i>
Pogge or armed bullhead	<i>Agonus cataphractus</i>
Pondweed	<i>Potamogeton</i>
Porgy	<i>Diplodus sargus</i>
Protozoa	<i>Entosiphon sulcatum</i> , Flagellate
Prussian carp	<i>Cyprinus carpio</i>

<u>Common Name</u>	<u>Scientific Name</u>
Pumpkinseed	<i>Lepomis gibbosus</i>
Purple sea urchin	<i>Strongylocentrotus purpuratus</i>
Rainbow trout	<i>Salmo gairdneri</i>
Red shiner	<i>Notropis lutrensis</i>
Roach	<i>Rutilus rutilus</i>
Rock bass	<i>Ambloplites rupestris</i>
Rotifer	<i>Keratella cochlearis</i> , Protozoa
Scud	<i>Gammarus fasciatus</i>
Sea perch	<i>Lutjanus</i> sp.
Sea urchin	<i>Echinometra</i> sp., <i>Arbacia punctulata</i>
Seaweed	<i>Fucus distichus</i> , <i>Fucus vesicullus</i>
Sheepshead minnow	<i>Cyprinodon variegatus</i>
Shiners	<i>Notropis</i> sp.
Shore crabs	<i>Carcinus maenas</i>
Shrimp	<i>Palaemonetes kadiakensis</i> , <i>Crangon</i> sp., <i>Pandalus</i> sp.
Sludge worm	Annelida
Smelt	<i>Osmerus</i> sp.
Snail	<i>Australorbis glabratus</i>
Sockeye salmon	<i>Oncorhynchus nerka</i>
Soft shell clam	<i>Mya arenaria</i>
Sponge	Porifera
Spot fin shiner	<i>Notropis spilopterus</i>
Spottail shiner	<i>Notropis hudsonius</i>
Starfish	Echinodermata
Stickleback (12-spined)	<i>Pygosteus pungitius</i>
Stonefly	<i>Claasenia sabulosa</i> , <i>Pteronarcella badia</i> , <i>Pteronarcys</i> sp., <i>Pteronarcys californica</i>
Striped bass	<i>Morone saxatilis</i>
Sunfish (common)	<i>Lepomis humilis</i>
Tench	<i>Tinca tinca</i>
Three-spined stickleback	<i>Gasterosteus aculeatus</i>
Vector snail	Gastropoda
Walleye	<i>Stizostedion vitreum</i>
Water beetle	Hemiptera
Water boatmen	Corixidae
Water flea	<i>Daphnia magna</i> , <i>Daphnia pulex</i>
Water shrimp	<i>Gammarus pulex</i>
Wheat	<i>Triticum aestivum</i>
Whitefish	<i>Coregonus</i> sp.
Winter-flounder	<i>Pseudopleuronectes americanus</i>
Worm	Annelida, <i>Nereis</i> sp.
Yellow perch	<i>Perca fluviatilis flavescens</i>

Scientific NameCommon Name

<i>Abramis brama</i>	Bream
<i>Agonus cataphractus</i>	Pogge or armed bullhead
<i>Alburnus alburnus</i>	Bleak
<i>Alosa sapidissima</i>	American shad
<i>Ambloplites rupestris</i>	Rock bass
<i>Anabaena</i> sp.	Blue-green algae
<i>Anguilla japonica</i>	Japanese eel
<i>Anguilla rostrata</i>	American eel
<i>Anguilla vulgaris</i>	Eel
Odonata	Dragonflies
Annelida	Worms
<i>Apis mellifera</i>	Honey bee
Arachnida	Daddy longlegs
<i>Arbacia punctulata</i>	Sea urchin
<i>Artemia salina</i>	Brine shrimp
<i>Aspergillus niger</i>	Fungus
<i>Australorbis glabratus</i>	Snail
<i>A. falcatus</i>	Green algae
<i>Bufo bufo</i>	Common toad
<i>Callinectes sapidus</i>	Blue crab
<i>Cancer franciscorum</i>	Crab
<i>Cancer magister</i>	Dungeness crab
<i>Carassius auratus</i>	Goldfish
<i>Carcinus maenas</i>	Shore crabs
<i>Cerastoderma edule</i>	Cockle
<i>Ceratopogonidae</i>	Phantom midge
<i>Chironomus plumosus</i>	Midge
<i>Chlorella pyrenoidosa</i> ,	
<i>Chlorella vulgaris</i>	Green algae
<i>Claassenia sabulosa</i>	Stonefly
<i>Cladophora</i>	Green algae
<i>Clupea harengus</i>	Herring
<i>Clupea pallasii</i>	Pacific herring
<i>Coregonus</i> sp.	Whitefish
Corixidae	Water boatmen
<i>Crangon crangon</i>	Brown shrimp
<i>Crassostrea gigas</i>	Pacific oyster
<i>Crassostrea virginica</i>	American oyster
<i>Cyprinodon variegatus</i>	Sheepshead minnow
<i>Cyprinus carpio</i>	Prussian carp
<i>Daphnia magna</i> , <i>Daphnia pulex</i>	Water flea
<i>Diplodus sargus</i>	Porgy
<i>Drosophila melanogaster</i>	Fruitfly
Echinodermata	Starfish
<i>Echinometra</i> sp.	Sea urchin
<i>Eliminus modestus</i>	Barnacles
<i>Engraulis mordax</i>	Northern anchovy
<i>Entosiphon sulcatum</i>	Protozoa

<u>Scientific Name</u>	<u>Common Name</u>
<i>Ephemerella subvaria</i>	Mayfly
<i>Esox lucius</i>	Northern pike
<i>Esox</i> sp.	Pike
<i>E. coli</i> , <i>E. typhosa</i>	Bacteria
<i>Fucus distichus</i> , <i>Fucus vesicullus</i>	Seaweed
<i>Fundulus diaphanus</i>	Killifish
<i>Fundulus heteroclitus</i>	Mummichog
<i>Gadus morrhua</i>	Cod
<i>Gambusia affinis</i>	Mosquito fish
<i>Gammarus fasciatus</i>	Scud
<i>Gammarus pulex</i>	Water shrimp
<i>Gasterosteus aculeatus</i>	Three-spined stickleback
Gastropoda	Vector snail
<i>Globicephala</i> sp.	Pilot Whale
<i>Haliotes</i> sp.	Abalone
Hemiptera	Water beetle, diving beetle
Hippoglossidae	Flounder
<i>Hippolyte zostericola</i>	Grass shrimp
Hirundinea	Leech
<i>Homarus americanus</i>	Northern lobster
<i>Ictalurus nebulosus</i>	Catfish (Brown bullhead)
<i>Ictalurus punctatus</i>	Channel catfish
<i>Keratella cochlearis</i>	Rotifer
<i>Lagodon rhomboides</i>	Marine pin perch, pinfish
<i>Laminaria digitata</i>	Atlantic kelp
<i>Lebistes reticulatus</i>	Guppy
<i>Lepidium sativum</i>	Garden cress
<i>Lepomis cyanellus</i>	Green sunfish
<i>Lepomis gibbosus</i>	Pumpkinseed
<i>Lepomis humilis</i>	Sunfish (common)
<i>Lepomis macrochirus</i>	Bluegill
<i>Leuciscus leuciscus</i>	Dace
<i>Littorina</i> sp.	Periwinkle
<i>Lutjanis</i> sp.	Sea perch
<i>Macrocystis pyrifera</i>	Kelp
<i>Macrozoarces americanus</i>	Ocean pout
<i>Menidia menidia</i>	Atlantic silverside
<i>Mercenaria mercenaria</i>	Hard clam
<i>Metapenaeus monoceros</i>	Penacid prawn
<i>Microcystis aeruginosa</i>	Blue-green algae
<i>Micropogon undulatus</i>	Croaker
<i>Micropterus salmoides</i>	Largemouth bass
<i>Morone saxatilis</i>	Striped bass

<u>Scientific Name</u>	<u>Common Name</u>
<i>Mugil cephalus</i>	Mullet
<i>Musca domestica</i>	Housefly
<i>Mya arenaria</i>	Soft shell clam
<i>Mysidaceae</i>	Mysid shrimp
<i>Mytilus edulis</i>	Mussel, marine mussel
<i>Nereis</i> sp.	Worms
<i>Nitzschia linearis</i>	Marine diatom
<i>Notemigonus crysoleucas</i>	Golden shiners
<i>Notropis hudsonius</i>	Spottail shiner
<i>Notropis lutrensis</i>	Red shiner
<i>Notropis atherinoides</i>	Emerald shiner
<i>Notropis</i> sp.	Shiners
<i>Notropis spilopterus</i>	Spot fin shiner
<i>Oncorhynchus kisutch</i>	Coho salmon
<i>Oncorhynchus tshawytscha</i>	Chinook salmon, King salmon
<i>Oncorhynchus nerka</i>	Sockeye salmon
<i>Oryzias latipes</i>	Japanese medaka
<i>Osmerus</i> sp.	Smelt
<i>Ostreidae</i>	Oysters
<i>Palaemonetes kadiakensis</i> , <i>Palaemonetes pugio</i>	Shrimp
<i>Panulirus japonicus</i>	Japanese Lobster
<i>Parophrys vetulus</i>	English sole
<i>Pelecypoda</i>	Marsh clam
<i>Perca fluviatilis</i>	Perch
<i>Perca fluviatilis flavescens</i>	Yellow perch
<i>P. fluorescens</i>	Bacteria
<i>Phaeodactylum tricornutum</i>	Diatom
<i>Phaseolus vulgaris</i>	Bush bean
<i>Phoxinus phoxinus</i>	Minnow
<i>Pimephales notatus</i>	Bluntnose minnow
<i>Pimephales promelas</i>	Fathead minnow
<i>Pleuronectes platessa</i>	Plaice
<i>Polycelis nigra</i>	Planarian worm
<i>Pomatomus saltatrix</i>	Bluefish
<i>Porifera</i>	Sponge
<i>Potamogeton</i>	Pondweed
<i>Protothaca staminea</i>	Little neck clam
<i>Pseudomonas putida</i>	Bacteria
<i>Pseudopleuronectes americanus</i>	Winter-flounder
<i>Pteronarcella badia</i> , <i>Pteronarcys californica</i> ,	Stonefly
<i>Pteronarcys</i> sp.	
<i>Pygosteus pungitius</i>	Stickleback (12-spined)
<i>Rana catesbiana</i>	Bullfrog
<i>Rana pipiens</i>	Leopard frog
<i>Rutilus rutilus</i>	Roach

<u>Scientific Name</u>	<u>Common Name</u>
<i>Salientia</i>	Frog
<i>Salmo clarki</i>	Cutthroat trout
<i>Salmo gairdneri</i>	Rainbow trout
<i>Salmo salar</i>	Atlantic salmon
<i>Salmo trutta</i>	Brook trout
<i>Salvelinus fontinalis</i>	Brook trout
<i>Salvelinus namaycush</i>	Lake trout
<i>Scenedesmus obliquus</i>	Algae
<i>Scenedesmus quadricauda</i>	Green algae
<i>Semotilus atromaculatus</i>	Creek chub
<i>Simocephalus</i> sp.	Daphnid
<i>Skeletonema costatum</i>	Diatom
<i>Squalius cephalus</i>	Chub
<i>Stenonema</i> sp.	Caddisflies
<i>Stizostedion vitreum</i>	Pickering, walleye
<i>Stolephorus purpureus</i>	Anchovy
<i>Strongylocentrotus purpurateus</i>	Purple sea urchin
<i>Tinca tinca</i>	Tench
<i>Triticum aestivum</i>	Wheat
<i>Venus mercenaria</i>	American hardshell clam
<i>Zygoptera</i>	Damselfly

## **7 HUMAN HEALTH**

### **7.1 Overview and Objectives**

The Human Health sections of the EnviroTIPS manuals present information pertaining to the effects on the human species and the effects on nonhuman mammalian species (to support interpretation of the human data where appropriate) as a result of exposure to each substance.

In order to provide a representative summary of material in the published literature for each Human Health chapter, standard references were gleaned for data related to skin and eye contact, and inhalation and ingestion effects, forms of contact which may result due to human exposure in the event of problem spills.

Qualitative and quantitative material have been included in the chapters. Acceptable occupational exposure levels in the form of time-weighted average exposure values and short-term exposure limits designated by governments and other agencies have been listed in Section 7.1 under the title Recommended Exposure Limits. Each chapter also contains reported human taste threshold and odour threshold values, when available in the literature (Section 7.3). Sections 7.2 and 7.4 present reported exposure levels and durations of contact with the substance, and the resulting effects due to skin and eye contact and inhalation and ingestion exposures for both humans and animals. In addition, a separate catalogue of human symptoms for each of the four routes of exposure is given in Section 7.5. The final section for each chapter deals with the human toxicity of decay or combustion products of the substance stressing acute toxicity effects.

### **7.2 Sources of Information**

Sources of information for the Human Health chapters were generally secondary and tertiary forms of the published literature. Printed documents and online information sources (TDB on-line) were used. Material from corporate authors, private industry, government and nongovernment agencies and personal authors were used. The information presented in the Human Health section reflects the literature; no attempt was made to verify the accuracy of the data reported. However, only those data sources thought to be reputable and reasonably validated were relied upon.

### **7.3 Glossary**

Absolute Odour Threshold	the concentration at which 50 percent of a panel of judges detected an odour
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ACGIH	American Conference of Governmental and Industrial Hygienists
Ceiling (Threshold Limit Value - C)	the concentration that should not be exceeded even instantaneously
CNS	Central Nervous System
Maximum Concentration	the maximum concentration is measured in a consecutive period of 15 minutes
Mean Concentration	the mean concentration is calculated using composite or continuous sampling of a minimum period of 2 hours or using five samples with sampling periods as mentioned in Section 13 of this by-law, the sampling being equally distributed in an 8-hour working day
EPA TSCA	Environmental Protection Agency/Toxic Substances Control Act (Note: Substances reported in the EPA TSCA inventory include those that are produced commercially or imported into the United States and have been added to the inventory in accordance with the provisions of the Toxic Substances Control Act) (RTECS 1979)
FEV	Forced Expiratory Volume
IDLH	Immediately Dangerous to Life and Health; concentration which represents a maximum level from which one could escape within 30 minutes without any impairing symptoms or any irreversible health effects (NIOSH Guide 1978)
Individual Perception Threshold	the lowest concentration of a particular odour at which a subject gave both an initial positive response and a repeated response when the same stimulus was given a second time (AAR 1981)
LC <sub>50</sub>	Lethal Concentration Fifty - a calculated concentration of a substance in air, exposure to which for a specified length of time is expected to cause the death of 50 percent of an entire defined experimental animal population, it is determined from the exposure to the substance of a significant number from that population (RTECS 1979)
LC <sub>LO</sub>	Lethal Concentration Low - the lowest concentration of a substance in air, other than LC <sub>50</sub> , which has been reported to have caused death in humans or animals (RTECS 1979)
LD <sub>50</sub>	Lethal Dose Fifty - a calculated dose of a substance which is expected to cause the death of 50 percent of an entire defined experimental animal population, it is determined from the exposure to the substance by any route other than inhalation of a significant number from that population (RTECS 1979)
LD <sub>LO</sub>	Lethal Dose Low - the lowest dose (other than LD <sub>50</sub> ) of a substance introduced by any route, other than inhalation, over any given period of time in one or more divided portions and reported to have caused death in humans or animals (RTECS 1979)

Lower Taste Threshold	the lowest concentration of the material which can be tasted (AAR 1981)												
MAC	Maximum Allowable Concentration												
MAK (Federal Republic of Germany)	maximum worksite concentration, 8 hours per day, 45 hours per week (ILO 1980)												
MAK-D (German Democratic Republic)	maximum average concentration allowed for a working shift of 8 hours and 45 minutes per day (ILO 1980)												
MAK-K (German Democratic Republic)	maximum concentration allowed for a short-term exposure not exceeding 30 minutes (ILO 1980)												
Median Recognition Threshold	the concentration at which 50 percent of the panel defined the odour as representative of the material (AAR 1981)												
Median Taste Threshold	the concentration which can be tasted by 50 percent of a panel of judges (AAR 1981)												
NCI	U.S. National Cancer Institute (note that selection of a chemical for bioassay does not necessarily imply that it is a carcinogen and that a compound originally scheduled for bioassay may be withdrawn from the NCI programme before testing actually begins) (RTECS 1979)												
NIOSH	U.S. National Institute for Occupational Safety and Health												
Odour Index	<p>a dimensionless term which indicates how readily the material can be smelled; it is the ratio of the driving force to introduce the material into the air to the ability of the material to create a recognized response, the odour index is computed from:</p> $\text{O.I.} = 1315.12 (P) (\text{U.R.T.})^{-1}$ <p>where</p> <table><tr><td>O.I.</td><td>=</td><td>odour index</td></tr><tr><td>P</td><td>=</td><td>vapour pressure (mm Hg)</td></tr><tr><td>U.R.T.</td><td>=</td><td>upper recognition threshold (ppm)</td></tr><tr><td>1315.12</td><td>=</td><td>conversion for vapour pressure from mm Hg to ppm (AAR 1981)</td></tr></table>	O.I.	=	odour index	P	=	vapour pressure (mm Hg)	U.R.T.	=	upper recognition threshold (ppm)	1315.12	=	conversion for vapour pressure from mm Hg to ppm (AAR 1981)
O.I.	=	odour index											
P	=	vapour pressure (mm Hg)											
U.R.T.	=	upper recognition threshold (ppm)											
1315.12	=	conversion for vapour pressure from mm Hg to ppm (AAR 1981)											
OSHA	Occupational Safety and Health Administration, U.S. Department of Labor												
PEL	Permissible Exposure Limit - a work-shift time-weighted average												

Population Perception Threshold	the concentration at which 50 to 100 percent of the population can identify and describe the odour or compare its quality with another odour (AAR 1981)
Short-Term Exposure Limits (Maximum Time/Maximum Concentration)	the maximum time for which unprotected personnel may be exposed to the specified maximum concentration of material (CHRIS 1978)
Skin	the TLV® of a substance, following by the designation "Skin", refers to the potential contribution to the overall exposure by the cutaneous route including mucous membranes and eyes, either by airborne or more particularly by direct contact with the substance; the designation is intended to suggest appropriate measures for the prevention of cutaneous absorption so that the threshold limit is not invalidated (TLV 1981)
STEC	Short-term Exposure Criteria - the maximum concentrations of agents in the air to which workers may be exposed from time to time; however, the exposure of workers to these maximum concentrations should be for not more than 15 minutes; not oftener than 4 times in a work day; and only after 60 minutes have elapsed from the time of the last previous exposure to such concentration (Ontario 1981)
STEL	Threshold Limit Value - Short-term Exposure Limit - the concentration to which workers can be exposed continuously for a short period of time without suffering from irritation, chronic or irreversible tissue change, or narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or materially reduce work efficiency, and provided that the daily TLV® - TWA also is not exceeded (TLV 1981)
STIL	Short-Term Inhalation Limit (CHRIS 1978)
TC <sub>LO</sub>	Toxic Concentration Low - the lowest concentration of a substance in air to which humans or animals have been exposed for any given period of time that has produced any toxic effect in humans or produced a carcinogenic, neoplastigenic or teratogenic effect in animals or humans (RTECS 1979)
TD <sub>LO</sub>	Toxic Dose Low - the lowest dose of a substance, introduced by any route other than inhalation, over any given period of time and reported to produce any toxic effect in humans or to produce carcinogenic, neoplastigenic or teratogenic effects in animals or humans (RTECS 1979)
Threshold Odour Concentration	the lowest concentration in air at which the odour of the material can be detected and/or recognized (AAR 1981)
TLV	Threshold Limit Value

TLV*	the time-weighted average concentration established by the American Conference of Governmental Industrial Hygienists for a normal 8-hour workday and a 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect (TLV 1981)
TOC	Threshold Odour Concentration
TWA	Time-weighted Average
TWAEc	Time-weighted Average Exposure Criteria - time-weighted average concentrations or levels of an agent for a 40-hour work week to which it is believed nearly all workers may be exposed day after day without experiencing adverse effects (Ontario 1981)
Upper Recognition Threshold	the concentration at which 100 percent of the panel defined the odour as representative of the material (AAR 1981)
Upper Taste Threshold	the concentration which can be tasted by the entire test population (AAR 1981)

## **8           CHEMICAL COMPATIBILITY**

### **8.1        Overview and Objectives**

This section is intended to provide a guide to the chemistry that could cause additional hazards in the case of a spill. Some examples are obvious - heat plus explosives, fire plus fuel - others are less so. Rather than attempting to estimate the probability of specific reactions under specific conditions, documented instances of reactivity of each chemical have been tabulated to form a catalogue of known hazardous reactions in a compact, usable form. In this way, the reactivity of each substance with a wide variety of others can be ascertained quickly, and appropriate precautions can be taken where a problem is apparent. This approach necessarily provides only an outline of the hazard to be expected; where planning requires more detail, additional information must be sought either from the sources referenced or from the manufacturer of the substance.

### **8.2        Information Sources**

Compatibility data was derived largely from these sources: Bretherick's "Handbook of Reactive Chemical Hazards", the National Fire Prevention Association's "Fire Prevention Guide on Hazardous Materials", and "A Method for Determining the Compatibility of Hazardous Wastes" (EPA 600/2-80-076). Reactivity with construction materials is included in Section 4.

## **9 SPILL COUNTERMEASURES**

### **9.1 Overview and Objectives**

In spill circumstances, response organizations must consider human health and safety, property, and environmental threats, both from a first response or emergency standpoint and that of long-term protection or countermeasures. Every spill is different; however, general response principles pertinent to specific chemical types are recognized. These general principles are discussed in this section of this report.

In many cases, a general guideline for a chemical may be found to be inappropriate under specific circumstances. The effects of very high or low temperatures may radically alter the degree of hazard posed by a spill and the measures or equipment suited for coping with it. High winds or waters may prohibit use of some containment measures. Spills involving coreactants may produce problems of an unforeseen nature. Rather than attempting to describe appropriate responses to specific spill circumstances, guides to response considering the salient properties of each substance have been prepared.

### **9.2 Information Sources**

Response organizations, industry experts, industry associations and the spill literature have all contributed to the information in this section. Where specific measures are recommended, they have been taken from the literature.

Suitable protective measures have been abstracted from different literature sources: NIOSH/OSHA's "Occupational Health Guidelines for Chemical Hazards", General Electric Company's "Material Safety Data Sheets", Oil and Hazardous Materials Technical Assistance Data System's "Information Sheets", National Safety Council's "Data Sheets", and Publication EE-20, "A Survey of Self-Contained Breathing Apparatus and Totally-Encapsulated Chemical Protection Suits".

### **9.3 Selection and Derivation of Data**

**9.3.1 Carbon Adsorption.** Recommendations for the removal of materials by activated carbon adsorption have been quoted. These recommendations are based on removal efficiencies calculated from experimentally measured adsorption data. The general measurement procedure has been to use various carbon dosages to treat water with known contaminant levels, and compare the contaminant levels in treated and untreated water. The procedure requires a standardized carbon type and screen size, with consistent contact times and dosages.

The adsorption process in dilute solutions has been found in general to be adequately described by the Freundlich equation:

$$X/M = KC_f^{1/n} \quad (1)$$

where  $X = C_o - C_f$  = amount of compound adsorbed from a given volume of solution

$M$  = weight of activated carbon

$C_o$  = amount of compound in untreated solution

$C_f$  = amount of compound in treated solution

$K, 1/n$  = empirical constants, characteristics of the compound and the carbon used

As the equation indicates, the loading on the carbon,  $X/M$ , is a function of the equilibrium concentration of an organic compound after carbon treatment. When  $X/M$  is plotted versus  $C_f$  on logarithmic paper,  $K$  is the  $X/M$  intercept at  $C_f = 1$  and  $1/n$  is the slope. A plot for the adsorption of benzidine dihydrochloride illustrates this (Figure 16).

The Freundlich equation can be rearranged to calculate the carbon dose required to reduce any initial concentration of compound to some predetermined residual concentration:

$$\frac{C_o - C_f}{M} = KC_f^{1/n} \quad (2)$$

This can be solved directly for the carbon dose required, or the equation can be rearranged to the logarithmic form:

$$\log (C_o - C_f) - \log M = \log K + 1/n \log C_f \quad (3)$$

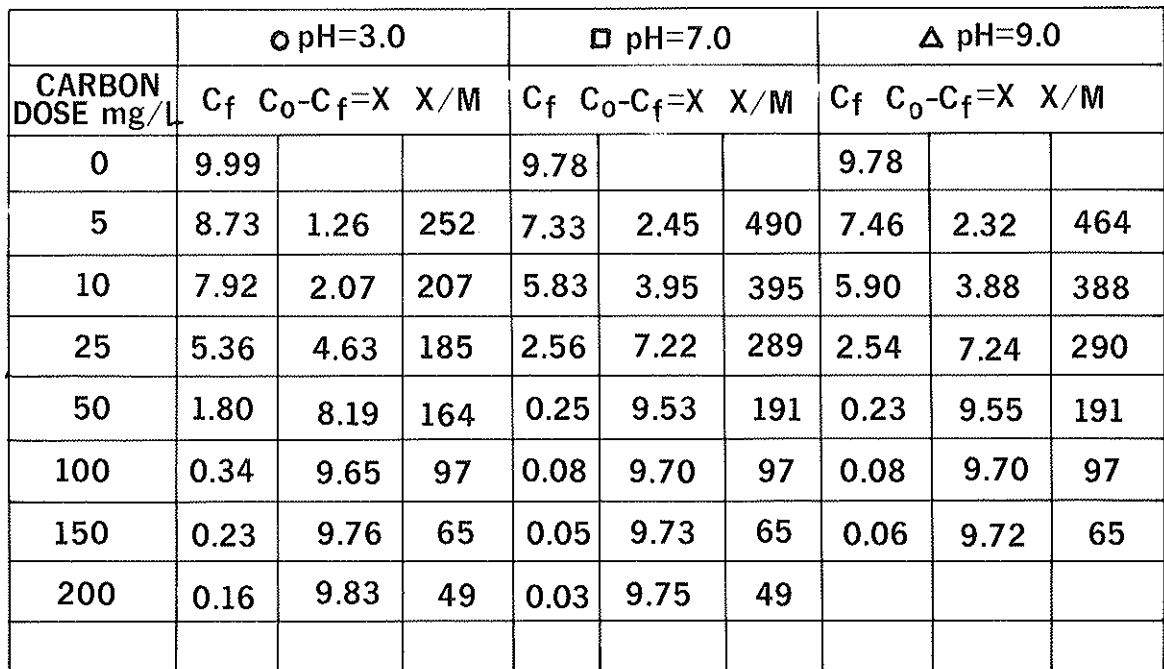
For example, this form may be used to calculate the carbon required to reduce benzidine dihydrochloride concentration from 10 mg/L to 0.1 mg/L using values for the constants from the preceding graph:

$$K = 220, 1/n = 0.37$$

$$\log (10 - 0.1) - \log M = \log 220 + 0.37 \log 0.1$$

$$M = 0.100 \text{ g/L or } 100 \text{ mg/L}$$

### EXAMPLE OF A CARBON ADSORPTION CURVE





Further calculated carbon requirements versus various variables are shown below:

Freundlich Parameters			
K = 110 1/n = 0.35		K = 220 1/n = 0.37	
Initial Conc. (mg/L)	pH = 3.0	Adsorption Capacity (mg/g)	pH = 7 and 9
10	250		520
1.0	110		220
0.1	51		97
0.01	23		42

CALCULATED CARBON REQUIREMENTS TO ACHIEVE INDICATED CHANGE IN CONCENTRATION (Carbon doses in mg/L at neutral pH)

Single Stage Powdered Carbon				Granular Carbon Column	
$C_f$ (mg/L)				$C_p$ (mg/L)	
$C_o$ (mg/L)	0.1	0.01	0.001	$C_o$ (mg/L)	breakthrough
1.0	9.4	24	58	1.0	4.5
0.1		2.2	5.7	0.1	1.0
0.01			0.52	0.01	0.2

The tabulated carbon doses illustrate the benefit of more than one stage of treatment. For benzidine dihydrochloride, to reduce an initial concentration of 10 mg/L to 0.1 mg/L in a single stage requires 100 mg/L of activated carbon. If removal is accomplished in two stages, i.e., 10 mg/L to 1.0 mg/L in the first stage followed by 1.0 mg/L to 0.1 mg/L in a second stage, the carbon dose is 40 mg/L + 9.4 mg/L = 49.4 mg/L of carbon, about one-half the dose required for a single stage process.

The ultimate number of stages in a carbon adsorption system is achieved in column operation. To estimate the granular carbon requirements for column operation, obtain the adsorption capacity from the isotherm plot for the concentration of compound to be treated. This capacity, designated  $(X/M)_{C_o}$ , is the ultimate capacity of the carbon

for the adsorbate at that concentration ( $C_0$ ). This capacity represents the ultimate loading for a single component solution that can be attained during granular carbon column treatment, if the column is operated until the adsorbate concentration in the effluent is equal to that of the influent. Granular carbon requirement ( $G_C$ ) can be calculated from the following equation:

$$G_C = \frac{C_0}{(X/M)C_0} \quad (4)$$

For the case of granular carbon treatment of a solution containing 1 mg/L of benzidine dihydrochloride ( $C_0 = 1.0$  mg/L;  $X/M = 220$  mg/g), solution of equation 4 yields:

$$G_C = \frac{1}{220} = 0.0045 \text{ g/L or } 4.5 \text{ mg/L}$$

Activated carbon exhibits a broad range of effectiveness in adsorbing organic compounds. Low-molecular-weight compounds with polar characteristics are not adsorbed well, if at all. Pesticides, polychlorinated biphenyls, polynuclear aromatic hydrocarbons, phthalates, aromatic, and substituted aromatic compounds are strongly adsorbed on activated carbon (EPA 600/8-80-023).

**9.3.2 Protective Measures.** The protective measures listed in the Countermeasures sections of the manuals have been recommended for personnel working in areas where the chemical is present and does not specifically mean that one may enter a chemical spill situation and be totally protected from contact and inhalation of the chemical involved. The data presented can be used as a guide to possible protective measures for use in spill circumstances.

## **10        PREVIOUS SPILL EXPERIENCE**

### **10.1       Overview and Objectives**

The objective of this section is to review spills which provide case-study information useful in planning spill response. The intent is to select incidents that have added to spill response knowledge or science. These are not necessarily the incidents of the highest degree of hazard, frequency of occurrence, or public profile. The emphasis in the discussion is on the response techniques and their effectiveness. Where applicable, comments, conclusions and recommendations have been included.

### **10.2       Information Sources**

The response information in this manual has been derived from publications dealing with hazardous materials or chemical spills, news reports, incident reports, and personal communication with various spill contractors and governmental agencies in Canada and the United States. In the cases of many chemicals, spills have occurred but response and cleanup techniques have not been recorded. In these cases, no spill experience is discussed.

## **11 ANALYTICAL METHODS**

### **11.1 Overview and Objectives**

The Analytical Methods sections of the EnviroTIPS manuals present standard or officially recommended methods for analyzing each substance in each environmental medium - air, water and soil. The level of detail presented is intended to acquaint the reader with the specific analytical hardware requirements for each substance. Detection limits, names, chromatographic packing materials, and so on, are included to indicate potential requirements for support of field needs. Samples of air, water and soil are presumed to be taken from the spill site and brought into a chemical laboratory for analysis.

The methods presented for each medium include both quantitative and qualitative analyses. The qualitative methods are generally faster, easier, less sensitive and less specific, and are used to determine if the substance is present. The quantitative methods are more accurate and precise.

Although it is recognized that some field methods of analysis exist or are under development, these were not included because of the relative newness of this field. Many methodologies and equipment are undergoing rapid changes and thus are difficult to document.

### **11.2 Sources of Information and Selection of Data**

The analytical methods for each substance were chosen from sources of standard or recommended methods. Wherever possible, the most simple, reliable and specific methods were chosen. These methods are usable in a chemical laboratory remote from the spill site.

No attempt was made to carry out an exhaustive literature review or to present methods requiring advanced, research-quality instrumentation. The simplest reliable method is suggested first, followed by more complex methods for increased reliability or specificity.

### **11.3 Approach for Each Medium**

**11.3.1 Air.** The analytical methods for airborne materials were most often taken from the U.S. National Institute for Occupational Safety and Health (NIOSH), the American Public Health Association (APHA), and the U.S. Environmental Protection Agency (EPA).

Air samples are usually collected by drawing air through solutions in impingers or through sampling tubes packed with activated carbon or porous polymer resin adsorbents, or by collecting air samples in gas sampling bags. The samples are analyzed using various techniques specific to the substance being sought.

**11.3.2 Water.** The methods for the analysis of the chemicals in water were most often taken from the American Society for Testing and Materials (ASTM), the American Water Works Association (AWWA), and the U.S. Environmental Protection Agency.

A representative sample of water, usually 1 litre, is collected in an appropriate container. Plastic containers are generally used for inorganic chemicals while glass is used for organics. The samples are kept cool during transportation to the laboratory.

**11.3.3 Soil.** The methods for the determination of the substances in soil were most frequently taken from ASTM, AWWA and "A Textbook of Soil Chemical Analysis" (Hesse 1972).

Representative samples of soil are collected in glass or plastic jars as specified by the method. They are ground in the laboratory into pieces of a size specified in the method and homogenized to ensure a representative sample. Various analytical methods, specific to the substance being sought, are used.

#### 11.4 Glossary

Absorption, Lambert's Law	<p>if <math>I_0</math> is the original intensity of an incident radiation, and <math>I</math> is the intensity after passing through a thickness "<math>x</math>" of a material whose absorption coefficient is <math>k</math>, <math>I = I_0 e^{-kx}</math></p> $\text{and absorption} = \log \frac{I_0}{I}$
Carbowax	tradename for polyethylene glycol and methoxypolyethylene glycol porous polymer resins; they are available in various molecular weights (e.g., $2 \times 10^4$ to $6 \times 10^6$ ) and are used as liquid phase support coatings in gas chromatography
Chromosorb	tradename for a series of screened calcined and flux-calcined diatomite particulate materials; they are used as stationary phase supports in gas-liquid chromatography
Chromatography	a laboratory analytical technique for the separation and identification of chemical compounds in complex mixtures; basically, it involves the flow of a mobile (gas or liquid) phase over a stationary phase (which may be a solid or a liquid). As the mobile phase

moves past the stationary phase, repeated adsorption and desorption of the solute occurs at a rate determined chiefly by its ratio of distribution between the two phases. If the ratio is large enough, the components of the mixture will move at different rates, producing a characteristic pattern, or chromatograph, from which their identity can be determined; liquid chromatography; gas chromatography; paper chromatography; thin-layer chromatography; ion-exchange chromatography; gel filtration are different forms

Colourimetry	an analytical technique based on measurement of the absorbance of a substance
Conductimetry	a technique of end point detection in a volumetric titration based on measurement of the conductance of the solution or determination of the concentration of an ionic analyte by its conductance
Desorption	the removal of a substance from a surface to which it is adsorbed; it may be accomplished by one or more of the following: heating, reduction of pressure, displacement by a more strongly adsorbed substance or dissolution by a solvent for which it has greater affinity
Digestion	the process in analytical chemistry of prolonged contact (usually with heating) of a mixture, to effect complete equilibrium of a reaction or physical process; used to "complete" extraction of materials, crystallization, adsorption processes; often refers to dissolution or extraction of particulate samples (e.g., soil or airborne particulate matter) by the above technique
Electron Capture Detector	a detector for gas chromatography; compounds with an electronegative group tend to capture electrons to form negative ions when exposed to a source of low-energy electrons; the negative ions are swept out through the carrier gas flow and are detected by the subsequent current reduction on an electrode
FFAP	Free Fatty Acid Phase - a liquid phase coated on a solid support used in gas-liquid chromatography
Flame Ionization Detector	a detector for gas chromatography; organic compounds, when pyrolyzed in a hydrogen-air flame, produce ionic species which allow electric current to be carried through the combustion gases; the ion current is measured and is proportional to the concentration of organic compounds
Fritted Glass	finely ground glass, sintered to form a porous, ceramic solid, used for filtering particulate matter from a liquid or gas stream
Impinger	a device containing an absorbing solution through which a stream of air is bubbled; versions for collecting a small volume of sample in a small liquid volume are called midjet impingers

Ion Chromatography	a chromatographic process where the stationary phase is an ion exchange medium (resin); resins are typically composed of a spherical polystyrene matrix crosslinked with divinylbenzene to which are bonded functional groups such as sulphonic acid or quarternary ammonium (a conductimetric detector is used)
Kovats Index	a relative retention index used to indicate where a compound will appear on a gas chromatogram with respect to n-paraffins
Mass Spectrometry	a method of chemical analysis in which ions created from the analyte substance by electron impact or chemical exchange are separated, identified and quantitated according to their mass. Ions are passed through a magnetic or an electrostatic field, or both; they are separated as they travel through the field at different velocities
Molal (m)	a concentration in which the amount of solute is stated in moles and the amount of solvent in kilograms (i.e., moles of solute per kilogram of solvent)
Molar (M)	a concentration in which one molecular weight in grams (1 mole) of a substance is dissolved in enough solvent to make 1 litre of solution
Normal (N)	a concentration in which one equivalent weight (molecular weight expressed as grams) of a substance is contained in 1 litre of solution; for example, a 2 N solution of nitric acid (MW = 63.0) contains $2 \times 63$ or 126 grams of nitric acid per litre
Qualitative Analysis	the identification of the constituents of a material irrespective of their amounts
Quantitative Analysis	the determination of the amounts in which the various constituents of a material are present
Reagent Blank	a solution or mixture of all reagents used in an analysis, treated in the same way as the sample but without the sample analyte present; provides a baseline correction to the result of the analysis
Retention Time	the time required for a solute peak to pass through a chromatographic column and reach the detector
Spectrometer	an instrument that disperses radiation and then records the resulting spectrum photoelectrically (e.g., emission, gamma-ray, x-ray or mass spectrometers)
Spectrophotometer	an instrument for observing spectra in the ultraviolet, visible, or infrared regions which allows quantitative determination of the light absorbed due to the analyte, thus permitting calculations of its concentration

Tenax GC	a proprietary porous linear polymer resin packing for gas chromatography, composed of poly <u>p</u> 2,6-diphenylphenylene oxide; it is stable to temperatures in excess of 400°C and is resistant to oxygen in the carrier gas
Thermal Conductivity Detector	a detector for a gas chromatograph which is based on changes in the thermal conductivity of the carrier gas stream caused by the presence of analyte substances
Titration	a method for determining volumetrically the concentration of a substance in solution by adding a standard solution of known volume and strength until the reaction is completed; the end-point of the reaction may be indicated visually by colourimetric methods or electrically by potentiometric, conductometric, or electrogravimetric methods
Triton	tradename for surfactants based on alkylaryl polyether alcohols, sulphonates and sulphates



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**INDEX**

<b>A</b>	<b>Page</b>
Absolute Odour Threshold	84
Absorption, Lambert's Law	97
ACGIH	85
Activated Carbon	90
Antoine Vapour Pressure Equation	6,14
Atmospheric Stability	32
Atomic Weight	6
Autoignition Temperature	6
Azeotrope	6
 <b>B</b>	
Behaviour in a Fire	7
Bhirud's Method	18
Bioconcentration Factor	75
BOD	75
Boiling Point	7
Bulk Density	7
Burning Characteristics	7
Burning Rate	7
 <b>C</b>	
Carbon Adsorption	90
Carbowax	97
Ceiling	85
Choked Flow	28
Chromosorb	97
Chromatography	97
Clapeyron Equation	18
CNS	85
COD	75
Coefficient of Thermal Expansion	7

	Page
Colourimetry	98
Combustible	5
Commerce	23
Compatibility	89
Compressibility Factor	7
Conductimetry	98
Constituent Components	7
Critical Pressure	7
Critical Temperature	7
Cylinders	24
<b>D</b>	
Darcy Equation	70
Decomposition Temperature	7
Density	7
Deflagration Point	7
Desorption	98
Detonation Point	8
Detonation Velocity	8
Dielectric Constant	8
Diffusion (in water)	64
Diffusivity	8
Digestion	97
Dilution	64
Dipole Moment	8
Dissociation Constant	8
Distillation Range	8
Drums	24
<b>E</b>	
Edminster Equation	19
Electrical Conductivity	8
Electron Capture Detector	98

	Page
Enthalpy	8
Entropy of Formation	8
EPA TSCA	85
Eutectic Composition	8
Evaporation	41,68
Evaporation Rate	8, 41,68
Explosiveness	8
<b>F</b>	
Fall Velocity	59
FEV	85
FFAP	98
Fire Properties	5
Fish (list of species)	76
Fishtine Equation	18
Flame Ionization Detector	98
Flame Speed	8
Flame Temperature	8
Flammable	5
Flammability	9
Flashback Potential	9
Flash Point	9
Free Energy of Formation	9
Freezing Point	9
Freundlich Equation	91
Fritted Glass	98
<b>G</b>	
Gaussian Plume Model	36
Gibb's Energy of Formation	9

	Page
<b>H</b>	
Hazard Zone Mapping	49
Health	84
Heat Capacity	9
Heat of Combustion	9
Heat of Crystallization	9
Heat of Decomposition	9
Heat of Dilution	9
Heat of Formation	9
Heat of Hydration	9
Heat of Polymerization	9
Heat of Solution	10
Heat of Transition	10
Heat of Vaporization	10
Henry's Law Constant	10
Hygroscopicity	10
Hydraulic Radius	64,65
<b>I</b>	
IDLH	85
Ignition Temperature	10
Impact Sensitivity	10
Impinger	98
Individual Perception Threshold	85
Insoluble	6
Interfacial Tension	10
Ion Chromatography	99
Ionization Constant	10
Ionization Potential	10
<b>K</b>	
Kistiakovskii Equation	15
Kovats Index	99



	Page
<b>L</b>	
Latent Heat of Fusion	10
Latent Heat of Sublimation	10
Latent Heat of Vaporization	15
Lateral Diffusion	38
Lattice Energy	10
LC	76
LD	76
Lead Block Test	10
Leak Nomograms	26
Liquid Density	18
Liquid Interfacial Tension	10, 11
Liquid Pool Radius	53
Lower Explosive Limit	11
Lower Flammability Limit	11
Lower Taste Threshold	86
<b>M</b>	
MAC	86
MAK	86
MAK-D,K	86
Mass Spectrometry	99
Maximum Concentration	85
Mean Concentration	85
Median Recognition Threshold	86
Median Taste Threshold	86
Melting Point	11
Miscible	6
Mixing	64
Moderately Soluble	6
Molal (m)	99
Molar (M)	99
Molar Volume	11
Molecular Weight	11

	Page
<b>N</b>	
NCI	86
NIOSH	86
Neutral Stability	32
Noncombustible	5
Normal (N)	99
<b>O</b>	
Octanol/Water Partition Coefficient	11
Odour Index	86
Organoleptic	76
OSHA	86
<b>P</b>	
Pasquill Plume	40
PEL	86
Penetration into Soil	69
Phase	13
Phase Diagrams	13
Plume Model	36
Polymerization Expansion	11
Polymerization Temperature	11
Pool Radius	54
Population Perception Threshold	87
Pour Point	11
Production	18
Puff Model	40
Punctures	27
<b>Q</b>	
Qualitative Analysis	99
Quantitative Analysis	99

## R

Railway Tank Cars	24
Reactions	89
Reagent Blank	99
Refractive Index	11
Releases	28
Resistivity	11
Retention Time	99
Roughness Coefficient	65

## S

Saturated Vapour Density	12
Saturation Concentration	11
Settling Time	61
Short-term Exposure Limits	87
Sinking	59
Skin	87
Slightly Soluble	6
Soluble	6
Solubility	12
Species	76
Specific Heat	12
Specific Heat Ratio	12
Specific Gravity	12
Spectrometer	99
Spectrophotometer	99
Spill Radius	59
Spreading	54
Standard Condition	12
State	12
STEC	87
STEL	87
STIL	87

	Page
Sublimation Point	12
Sublimation Temperature	12
Surface Tension	12

## Page

### T

Tank Cars	24
Tank Trucks	24
TC	87
TD	87
Tenax	100
Terminal Fall Velocity	60
Thermal Conductivity	12
Th.OD	76
Thermal Conductivity Detector	100
Threshold Odour Concentration	87
Thompson's Rule	15
Titration	100
Triton	100
TL <sub>m</sub>	76
TLV	87, 88
TOC	88
Transportation	24
Transition Point	12
Transition Temperature	12
Triple Point	12
TWA	88
TWAE	88

### U

Upper Explosive Limit	12
Upper Flammability Limit	12

	Page
Upper Recognition Threshold	88
Upper Taste Threshold	88
 <b>V</b>	
Vapour Density	13
Vapour Dispersion Nomograms	41
Vapour Emission Rate	41
Vapour Pressure	13
Vapour Weight-Volume Conversion Factor	13
Vapour Specific Gravity	13
Venting	27, 28
Vertical Diffusion	39
Virtual Point Source	37
Viscosity	13
Volume Increments	21
 <b>W</b>	
Watson Correlation	17
Weather Conditions	44



## LIST OF SUBSTANCES FOR WHICH ENVIROTIPS MANUALS HAVE BEEN PREPARED

Acetic Acid	Naphtha
Acetic Anhydride	Natural Gas
Ammonia	Nitric Acid
Ammonium Nitrate	Phenol
Ammonium Phosphates	Phosphoric Acid
Benzene	Phosphorus
Butyraldehydes	Polychlorinated Biphenyls (PCBs)
Calcium Chloride	Potash (Potassium Chloride)
Calcium Oxide/Hydroxide	Propylene
Carbon Dioxide	Propylene Oxide
Chlorine	Sodium Chlorate
Cyclohexane	Sodium Chloride
Ethylbenzene	Sodium Hydroxide
Ethylene	Sodium Hypochlorite
Ethylene Dichloride (1,2-Dichloroethane)	Sodium Sulphate
Ethylene Glycol	Styrene (Monomer)
Ethylene Oxide	Sulphur
2-Ethylhexanol	Sulphur Dioxide
Ferric Chloride	Sulphuric Acid (and Oleum)
Formaldehyde	Tetraethyl Lead
Hydrogen Chloride/Acid	Toluene
Hydrogen Fluoride/Acid	Urea
Hydrogen Sulphide	Vinyl Chloride
Mercury	Xylenes
Methanol	Zinc Sulphate
Morpholine	