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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

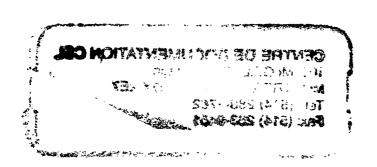
Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. This manual has been reviewed by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

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS



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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals which were spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their impact 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 these data are recommended by the Government of Canada, nor any other group.

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TABLE OF CONTENTS

| | | Page |
|---|---|--|
| FOREWO | DRD | i |
| ACKNO | WLEDGEMENTS | i |
| LIST OF | FIGURES | vii |
| LIST OF | TABLES | ix |
| 1 | SUMMARY | 1 |
| 2 | PHYSICAL AND CHEMICAL DATA | 3 |
| 3 | COMMERCE AND PRODUCTION | 10 |
| 3.1 3.2 3.3 3.4 3.5 3.5.1 3.5.2 3.6 3.7 3.8 | Grades, Purities Domestic Manufacturers Major Transportation Routes Production Levels Manufacture of Ethylene Dichloride Raw Materials Manufacturing Process Future Development Major Uses in Canada Major Buyers in Canada MATERIAL HANDLING AND COMPATIBILITY Containers and Transportation Vessels | 10 10 10 10 11 11 11 11 11 11 |
| 4.1.1 4.1.1.1 4.1.1.2 4.1.2 4.2 4.2.1 4.2.2 4.3 | Bulk Shipment Railway tank cars Tank motor vehicles Packaging Off-loading Off-loading Off-loading Equipment and Procedures for Railway Tank Cars Specifications and Materials for Off-loading Equipment Compatibility with Materials of Construction | 13 13 14 14 14 14 19 |
| 5 | CONTAMINANT TRANSPORT | 23 |
| 5.1 5.2 5.2.1 5.2.2 5.2.2.1 5.2.2.2 5.2.3 5.3 5.3.1 | General Summary Leak Nomograms Introduction Nomograms Figure 9: Percent remaining versus time Figure 10: Discharge rate versus time Sample Calculations Dispersion in the Air Introduction | 23 23 24 24 26 26 26 26 |

| 5.3.2.1 Figure 13: Vapour emission rate versus liquid pool radius for various temperatures 27 5.3.2.2 Figure 16: Vapour concentration versus downwind distance 31 5.3.2.3 Table 8: Maximum plume hazard half-widths 37 5.3.2.4 Figure 17: Plume travel time versus travel distance 37 5.3.3 Sample Calculation 37 5.4.1 Introduction 40 5.4.2.1 Zone of streambed contamination - no dissolution 43 5.4.2.1 Zone of streambed contamination - total dissolution 44 5.4.3.1 Zone of contamination on streambed 56 5.4.3.2 Pollutant concentration in non-tidal river 60 5.4.3.3 Average pollutant concentration in lakes or still water bodies 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA | | | Page |
|--|---------|--|------|
| various temperatures 27 5.3.2.2 Figure 14: Vapour concentration versus downwind distance 31 5.3.2.3 Table 8: Maximum plume hazard half-widths 33 5.3.3 Sample Calculation 37 5.4 Behaviour in Water 40 5.4.1 Introduction 40 5.4.2 Nomograms 43 5.4.2.1 Zone of streambed contamination - no dissolution 43 5.4.2.2 Downstream pollutant concentration - total dissolution 44 5.4.3.1 Zone of contamination on streambed 56 5.4.3.2 Pollutant concentration in non-tidal river 60 5.4.3.3 Average pollutant concentration in lakes or still water bodies 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Sample Calculation 64 | 5.3.2 | | 27 |
| 5.3.2.2 Figure 14: Vapour concentration versus downwind distance 31 5.3.2.3 Table 8: Maximum plume hazard half-widths 33 5.3.2.4 Figure 17: Plume travel time versus travel distance 37 5.3.3 Sample Calculation 37 5.4 Behaviour in Water 40 5.4.1 Introduction 40 5.4.2.1 Zone of streambed contamination - no dissolution 43 5.4.2.2 Downstream pollutant concentration - total dissolution 44 5.4.3.1 Zone of streambed contamination on streambed 56 5.4.3.2 Pollutant concentration in non-tidal river 60 5.4.3.3 Average pollutant concentration in lakes or still water bodies 61 5.4.3.2 Pollutant concentration in lakes or still water bodies 61 5.5.1 Introduction 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.4 Soils 62 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculat | 5.3.2.1 | | |
| 5.3.2.3 Table 8: Maximum plume hazard half-widths 33 5.3.2.4 Figure 17: Plume travel time versus travel distance 37 5.3.3 Sample Calculation 37 5.4 Behaviour in Water 40 5.4.1 Introduction 40 5.4.2.1 Nomograms 43 5.4.2.2 Downstream pollutant concentration - no dissolution 43 5.4.3.1 Zone of contamination on streambed 56 5.4.3.1 Zone of contamination in non-tidal river 56 5.4.3.1 Zone of contamination in non-tidal river 60 5.4.3.3 Average pollutant concentration in lakes or still water bodies 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5 Subsurface Behaviour: Penetration into Soil 62 5.5 Subsurface Behaviour: Penetration into Soil 62 5.5.1 Introduction 61 6.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 | | | |
| 5.3.2.4 Figure 17: Plume travel time versus travel distance 37 5.3.3 Sample Calculation 37 5.4 Behaviour in Water 40 5.4.1 Introduction 43 5.4.2 Nomograms 43 5.4.2.1 Zone of streambed contamination - no dissolution 43 5.4.2.2 Downstream pollutant concentration - total dissolution 44 5.4.3.1 Zone of contamination on streambed 56 5.4.3.2 Pollutant concentration in non-tidal river 60 5.4.3.3 Average pollutant concentration in lakes or still water bodies 61 5.5.1 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 | | | |
| 5.3.3 Sample Calculation 37 5.4 Behaviour in Water 40 5.4.1 Introduction 40 5.4.2.1 Zone of streambed contamination – no dissolution 43 5.4.2.1 Zone of streambed contamination – no dissolution 43 5.4.2.1 Zone of streambed contamination – total dissolution 44 5.4.3.2 Downstream pollutant concentration in total dissolution 56 5.4.3.2 Pollutant concentration in non-tidal river 60 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.1 Introduction 61 5.5.2 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6.1 Suggested or Regula | | | |
| 5.4 Behaviour in Water 40 5.4.1 Introduction 40 5.4.2.1 Zone of streambed contamination – no dissolution 43 5.4.2.2 Downstream pollutant concentration – total dissolution 43 5.4.3.1 Zone of contamination on streambed 56 5.4.3.2 Pollutant concentration in non-tidal river 60 5.4.3.3 Average pollutant concentration in lakes or still water bodies 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.2.2 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Logardati | | | |
| 5.4.1 Introduction 40 5.4.2.1 Nomograms 43 5.4.2.2.2 Downstream pollutant concentration – total dissolution 44 5.4.3.3 Sample Calculations 56 5.4.3.2.2 Pollutant concentration in streambed 56 5.4.3.3.2 Pollutant concentration in lakes or still water bodies 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.2.2 Aquatic Toxicity 70 6.2.3 Lu.S. Toxicity Rating 70 6.2.4 U.S. Toxicity Rating 70 6.3.1 Livestock 71 6.4. | | | |
| 5.4.2.1 Nomograms 43 5.4.2.1 Zone of streambed contamination – no dissolution 43 5.4.2.1 Downstream pollutant concentration – total dissolution 44 5.4.3.1 Sample Calculations 56 5.4.3.1 Zone of contamination on streambed 56 5.4.3.2 Pollutant concentration in non-tidal river 60 5.4.3.3 Average pollutant concentration in lakes or still water bodies 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 6.5 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1.1 Suggested or Regulated Limits 70 6.1.2 Air 70 6.1.2 Air 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Aquatic Toxicity <td></td> <td></td> <td></td> | | | |
| 5.4.2.1 Zone of streambed contamination - no dissolution 43 5.4.2.2 Downstream pollutant concentration - total dissolution 44 5.4.3.1 Zone of contamination on streambed 56 5.4.3.2 Pollutant concentration in non-tidal river 60 5.4.3.3.2 Average pollutant concentration in lakes or still water bodies 61 5.5.3 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Water 70 6.1.1 Water 70 6.1.2 Air 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 71 6.3 Toxicity to Other Biota 71 6.4.1 B-O.D. 72 | | | |
| 5.4.2.2 Downstream pollutant concentration – total dissolution 44 5.4.3.1 Sample Calculations 56 5.4.3.2 Pollutant concentration in non–tidal river 60 5.4.3.3 Average pollutant concentration in lakes or still water bodies 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.2.1 Aquatic Toxicity 70 6.2.2 Measured Toxicities 70 6.3 Toxicity Rating 70 6.4.1 Livestock 71 6.3.1 Livestock 71 6.4.2 Chemical Degradation 72 <td< td=""><td></td><td></td><td></td></td<> | | | |
| 5.4,3 Sample Calculations 56 5.4,3.1 Zone of contamination on streambed 56 5.4,3.2 Pollutant concentration in non-tidal river 60 5.4,3.3 Average pollutant concentration in lakes or still water bodies 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.4.2 Plants 72 6.4.3 Other St | | Zone of streambed contamination - no dissolution | |
| 5.4.3.1 Zone of contamination on streambed 56 5.4.3.2. Pollutant concentration in non-tidal river 60 5.4.3.3 Average pollutant concentration in lakes or still water bodies 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.1.3 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. | 5.4.2.2 | Downstream pollutant concentration - total dissolution | |
| 5.4.3.2 Pollutant concentration in non-tidal river 5.4.3.3 Average pollutant concentration in lakes or still water bodies 5.5 Subsurface Behaviour: Penetration into Soil 6.5.1 Introduction 6.5.2 Equations Describing Ethylene Dichloride Movement into Soil 6.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 6.5.4 Soils 6.5.5 Penetration Nomograms 6.4 Sample Calculation 6 ENVIRONMENTAL DATA 6.1 Suggested or Regulated Limits 6.1.1 Water 6.1.2 Air 6.2 Aquatic Toxicity 6.2.1 U.S. Toxicity Rating 6.2.2 Measured Toxicities 6.3 Toxicity to Other Biota 6.3.1 Livestock 6.3.1 Livestock 6.3.2 Plants 6.4 Degradation 6.4.4 Degradation 6.5 Long-term Fate and Effects 7 HUMAN HEAL TH 7 Recommended Exposure Limits 7.1 Recommended Exposure Limits 7.2 Irritation Data 7.3 Threshold Perception Properties 7 Takes Tail Recommended Exposure Part of the Properties Tail Part of the Properties Tail Part of the Properties Tail Part of the Properties 7 Threshold Perception Properties 7 Threshold Perception Properties | 5.4.3 | Sample Calculations | |
| 5.4,3.3 Average pollutant concentration in lakes or still water bodies 61 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.1.3 Water 70 6.1.4 U.S. Toxicity Rating 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4.2 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 | 5.4.3.1 | | |
| 5.5 Subsurface Behaviour: Penetration into Soil 61 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.1.1 Water 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate | 5.4.3.2 | Pollutant concentration in non-tidal river | 60 |
| 5.5.1 Introduction 61 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.2.2 Measured Toxicity Rating 70 6.2.2 Measured Toxicity 70 6.2.1 Livestock 71 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.4.2 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 </td <td>5.4.3.3</td> <td>Average pollutant concentration in lakes or still water bodies</td> <td>61</td> | 5.4.3.3 | Average pollutant concentration in lakes or still water bodies | 61 |
| 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil 62 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.1.2 Air 70 6.1.2 Aquatic Toxicity 70 6.1.2 Aquatic Toxicity Rating 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 7 HUMAN HEAL TH 73 <t< td=""><td>5.5</td><td>Subsurface Behaviour: Penetration into Soil</td><td>61</td></t<> | 5.5 | Subsurface Behaviour: Penetration into Soil | 61 |
| 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.2.1 Air 70 6.2.2 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 75 7.2.1 Skin Conta | 5.5.1 | Introduction | 61 |
| 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil 62 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 6.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.2.1 Air 70 6.2.2 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 75 7.2.1 Skin Conta | 5.5.2 | Equations Describing Ethylene Dichloride Movement into Soil | 62 |
| 5.5.4 Soils 64 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.2.1 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3.1 Odour 77 < | 5.5.3 | | 62 |
| 5.5.5 Penetration Nomograms 64 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.1.2 Air 70 6.2 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3.1 Odour 77 <td></td> <td></td> <td>64</td> | | | 64 |
| 5.5.6 Sample Calculation 64 6 ENVIRONMENTAL DATA 70 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.2.2 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3.1 Odour 77 | | Penetration Nomograms | 64 |
| 6.1 Suggested or Regulated Limits 70 6.1.1 Water 70 6.1.2 Air 70 6.2 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | | | 64 |
| 6.1.1 Water 70 6.1.2 Air 70 6.2 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6 | ENVIRONMENTAL DATA | 70 |
| 6.1.2 Air 70 6.2 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 L ivestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 L ong-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.1 | Suggested or Regulated Limits | |
| 6.2 Aquatic Toxicity 70 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2.1 Skin Contact 75 7.2.2 Eye Contact 75 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.1.1 | Water | |
| 6.2.1 U.S. Toxicity Rating 70 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.1.2 | Air | |
| 6.2.2 Measured Toxicities 70 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.2 | Aquatic Toxicity | .70 |
| 6.3 Toxicity to Other Biota 71 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.2.1 | U.S. Toxicity Rating | 70 |
| 6.3.1 Livestock 71 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.2.2 | Measured Toxicities | 70 |
| 6.3.2 Plants 71 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.3 | Toxicity to Other Biota | 71 |
| 6.4 Degradation 72 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.3.1 | Livestock | 71 |
| 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.3.2 | Plants | |
| 6.4.1 B.O.D. 72 6.4.2 Chemical Degradation 72 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.4 | Degradation | 72 |
| 6.4.3 Other Studies 72 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.4.1 | B.O.D. | 72 |
| 6.5 Long-term Fate and Effects 72 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.4.2 | Chemical Degradation | 72 |
| 7 HUMAN HEAL TH 73 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.4.3 | Other Studies | 72 |
| 7.1 Recommended Exposure Limits 73 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 6.5 | Long-term Fate and Effects | 72 |
| 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 7 | HUMAN HEAL TH | 73 |
| 7.2 Irritation Data 75 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 7.1 | Recommended Exposure Limits | 73 |
| 7.2.1 Skin Contact 75 7.2.2 Eye Contact 76 7.3 Threshold Perception Properties 77 7.3.1 Odour 77 | 7.2 | · · · · · · · · · · · · · · · · · · · | 75 |
| 7.2.2 Eye Contact 7.3 Threshold Perception Properties 7.3.1 Odour 7.3.1 7.3.1 | 7.2.1 | | |
| 7.3 Threshold Perception Properties 7.3.1 Odour 7.3.2 Threshold Perception Properties 7.7 | 7.2.2 | | |
| 7.3.1 Odour 77 | | | |
| | | | |
| 11/1 | 7.3.2 | Taste | 77 |

| | | Page |
|--------------|--|------|
| 7.4 | Long-term Studies | 78 |
| 7.4.1 | Inhalation | 78 |
| 7.4.2 | Ingestion | 82 |
| 7.4.3 | Skin Contact | 83 |
| 7.4.4 | Carcinogenicity | 84 |
| 7.4.5 | Mutagenicity and Teratogenicity | 85 |
| 7 . 5 | Symptoms of Exposure | 86 |
| 7.5.1 | Inhalation | 86 |
| 7.5.2 | Ingestion | 86 |
| 7.5.3 | Skin Contact | 87 |
| 7.5.4 | Eye Contact | 87 |
| 7.6 | Human Toxicity to Decay or Combustion Products | 87 |
| 7.6.1 | Carbon Monoxide, Carbon Dioxide, Phosgene, and | |
| | Hydrogen Chloride | 87 |
| 8 | CHEMICAL COMPATIBILITY | 89 |
| 8.1 | Compatibility of Ethylene Dichloride with | |
| | Other Chemicals and Chemical Groups | 89 |
| 9 | COUNTERMEASURES | 91 |
| 9.1 | Recommended Handling Procedures | 91 |
| 9.1.1 | Fire Concerns | 91 |
| 9.1.2 | Fire Extinguishing Agents | 91 |
| 9.1.3 | Spill Actions | 91 |
| 9.1.3.1 | General | 91 |
| 9.1.3.2 | Spills on land | 92 |
| 9.1.3.3 | Spills in water | 92 |
| 9.1.4 | Cleanup and Treatment | 92 |
| 9.1.4.1 | Spills on land | 92 |
| 9.1.4.2 | Spills in water | 92 |
| 9.1.4.3 | General | 92 |
| 9.1.5 | Disposal | 93 |
| 9.1.6 | Charcoal Filtration Data | 93 |
| 9.1.7 | Protective Measures | 94 |
| 9.1.8 | Special Precautions | 94 |
| 9.2 | Specialized Countermeasures Equipment, Materials | |
| , - | or Systems | 95 |
| 10 | PREVIOUS SPILL EXPERIENCE | 96 |
| 10.1 | Barge Spill | 96 |
| 11 | ANALYTICAL METHODS | 97 |
| 11.1 | Quantitative Method for the Detection of Ethylene Dichloride | |
| • • | in Air | 97 |
| 11.1.1 | Gas Chromatography | 97 |
| | . . , | |

| | | Page |
|--------|--|------|
| 11.2 | Qualitative Method for the Detection of Ethylene Dichloride | |
| | in Air | 98 |
| 11.3 | Quantitative Method for the Detection of Ethylene Dichloride | |
| | in Water | 98 |
| 11.3.1 | Partition Infrared | 98 |
| 11.4 | Qualitative Method for the Detection of Ethylene Dichloride | |
| | in Water | 98 |
| 11.5 | Quantitative Method for the Detection of Ethylene Dichloride | , 0 |
| **** | in Soil | 99 |
| 11.5.1 | Partition Infrared | 99 |
| 11.6 | Qualitative Method for the Detection of Ethylene Dichloride | // |
| 11.0 | in Soil | 99 |
| 12 | REFERENCES AND BIBLIOGRAPHY | 100 |
| 12.1 | References | 100 |
| 12.2 | Bibliography | 106 |

LIST OF FIGURES

| Figure | | Page |
|--------|---|------|
| 1 | VAPOUR PRESSURE vs TEMPERATURE | 7 |
| 2 | SOLUBILITY IN WATER vs TEMPERATURE | 7 |
| 3 | LIQUID DENSITY vs TEMPERATURE | 8 |
| 4 | LIQUID VISCOSITY vs TEMPERATURE | 8 |
| 5 | PHASE DIAGRAM | 9 |
| 6 | RAILWAY TANK CAR - CLASS 111A60W1 | 15 |
| 7 | TYPICAL DRUM CONTAINERS | 18 |
| 8 | TANK CAR WITH PUNCTURE HOLE IN BOTTOM | 24 |
| 9 | PERCENT REMAINING vs TIME | 25 |
| 10 | DISCHARGE RATE vs TIME | 25 |
| 11 | SCHEMATIC OF CONTAMINANT PLUME | 28 |
| 12 | FLOWCHART TO DETERMINE VAPOUR HAZARD ZONE | 29 |
| 13 | VAPOUR EMISSION RATE vs LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES | 30 |
| 14 | NORMALIZED VAPOUR CONCENTRATION vs DOWNWIND DISTANCE | 32 |
| 15 | CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³) | 34 |
| 16 | CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (Volume $\%$ to g/m ³) | 35 |
| 17 | PLUME TRAVEL TIME vs TRAVEL DISTANCE | 38 |
| 18 | EVACUATION AREA FOR STEADY WINDS, EXAMPLE PROBLEM | 41 |
| 19 | EVACUATION AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM | 41 |
| 20 | MAXIMUM SPILL RADIUS vs SPILL SIZE | 42 |
| 21 | FALL VELOCITY vs PUNCTURE SIZE | 45 |

viii

| Figure | | Page |
|--------|---|------|
| 22 | SETTLING TIME vs FALL VELOCITY | 46 |
| 23 | DISTANCE vs SETTLING TIME | 47 |
| 24 | SPILL WIDTH vs PUNCTURE SIZE | 48 |
| 25 | FLOWCHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVER | 50 |
| 26 | TIME vs DISTANCE | 51 |
| 27 | HYDRAULIC RADIUS vs CHANNEL WIDTH | 52 |
| 28 | DIFFUSION COEFFICIENT vs HYDRAULIC RADIUS | 53 |
| 29 | ALPHA vs DIFFUSION COEFFICIENT | 54 |
| 30 | ALPHA vs DELTA | 55 |
| 31 | MAXIMUM CONCENTRATION vs DELTA | 57 |
| 32 | VOLUME vs RADIUS | 58 |
| 33 | AVERAGE CONCENTRATION vs VOLUME | 59 |
| 34 | SCHEMATIC SOIL TRANSPORT | 63 |
| 35 | FLOWCHART FOR NOMOGRAM USE | 65 |
| 36 | PENETRATION IN COARSE SAND | 66 |
| 37 | PENETRATION IN SILTY SAND | 67 |
| 38 | PENETRATION IN CLAY TILL | 68 |

LIST OF TABLES

| Table | | Page |
|-------|--|------|
| 1 | CONVERSION NOMOGRAMS | 6 |
| 2 | RAIL WAY TANK CAR SPECIFICATIONS | 13 |
| 3 | TYPICAL RAIL WAY TANK CAR SPECIFICATIONS - CLASS 111A60W1 | 16 |
| 4 | DRUMS | 17 |
| 5 | COMPATIBILITY WITH MATERIALS OF CONSTRUCTION | 20 |
| 6 | MATERIALS OF CONSTRUCTION | 21 |
| 7 | WEATHER CONDITIONS | 33 |
| 8 | MAXIMUM PLUME HAZARD HALF-WIDTHS (for ethylene dichloride at 20°C) | 36 |

1 SUMMARY

ETHYLENE DICHLORIDE (C2H4Cl2)

Colourless liquid with a chloroform-like odour

SYNONYMS

1,2-Dichloroethane, Ethylene Chloride, EDC, Sym-Dichloroethane, Glycol Dichloride, Dutch Oil, Bichlorure d'Ethylene (Fr.)

IDENTIFICATION NUMBERS

UN No. 1184; CAS No. 107-06-2; OHM-TADS No. 7216717; STCC No. 4909166

GRADES & PURITIES

Commercial: 99.5 to 99.8 percent purity

IMMEDIATE CONCERNS

Fire: Flammable. Poisonous gases (hydrogen chloride, carbon monoxide, carbon dioxide

and phosgene) are produced in fire. Flashback may occur along vapour trail

Human Health: Moderately toxic by all routes

Environment: Harmful to aquatic life

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): liquid Density: 1.25 g/mL (20°C)

Boiling Point: 83.5°C Solubility (in water): 0.85 g/100 mL

Melting Point: -35.36°C Behaviour (in water): sinks

Flammability: flammable

Flash Point: 13°C (CC)

Vapour Pressure: 8.3 kPa (20°C)

Behaviour (in air): evaporates slowly
Odour Threshold Range: 6 to 40 ppm

ENVIRONMENTAL CONCERNS

Ethylene dichloride is dangerous to aquatic life in high concentrations. It is suspected to be bioaccumulative but this has not been firmly established. It is toxic to plants and microorganisms.

HUMAN HEALTH

TLV*: 10 ppm (40 mg/m^3)

IDLH: $1,000 \text{ ppm } (4,100 \text{ mg/m}^3)$

Exposure Effects

Inhalation: Inhalation of vapour causes nausea, vomiting, dizziness, and difficult

breathing. High concentrations may result in respiratory failure and death

Contact: Contact with liquid may produce transient corneal injury and burns to eyes. Prolonged contact with skin causes irritation. Liquid is absorbed readily, producing symptoms similar to inhalation

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "FLAMMABLE". Call fire department and notify manufacturer. Eliminate sources of ignition. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Use foam, dry chemical, or carbon dioxide to extinguish. Flashback may occur along vapour trail. Cool fire-exposed containers with water. Stay clear of tank ends.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill. Remove material with pumps or vacuum equipment. Sorb residual liquid on natural or synthetic sorbents. Recover undamaged containers

Water: Contain by damming or water diversion. Dredge or vacuum pump to remove contaminants, liquids and contaminated bottom sediments

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

NAS HAZARD RATING

| Category | Rating |
|--|--|
| Fire | 3 NFPA |
| Health | HAZARD |
| Vapour Irritant Liquid or Solid Irritant Poison | 2 CLASSIFICATION 2 3 |
| Water Pollution | Flammability |
| Human Toxicity Aquatic Toxicity Aesthetic Effect | 3 2 2 Health 2 0 Reactivity |
| Reactivity | X |
| Other Chemicals Water Self-reaction | 1 0 0 |

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance Colourless liquid (Dow MSDS 1980)

Usual shipping state Liquid (Dow MSDS 1980)

Physical state at 15°C, 1 atm Liquid

Freezing point -35.75°C (Ullmann 1975)
Melting point -35.36°C (CRC 1980)

Boiling point 83.47°C (CRC 1980; ISH 1977)

Vapour pressure 5.3 kPa (10°C) (CRC 1980)

8.5 kPa (20°C) (Ullmann 1975) 13.2 kPa (30°C) (ISH 1977)

Densities

Density 1.252 g/mL (20°C) (Ullmann 1975)

Specific gravity 1.250 (25°/25°C) (Dow MSDS 1980)

1.255 (20°C) (ISH 1977)

Vapour density 3.42 (Dow MSDS 1980)

3.88 g/L (boiling point) (ISH 1977; Ullmann

1975)

Fire Properties

Flammability Flammable liquid (NFPA 1978)

Flash point CC 13°C (NFPA 1978; Ullmann 1975)

OC 16°C (CHRIS 1978) 21°C (ISH 1977)

Autoignition temperature 413°C (NFPA 1978)

440°C (Ullmann 1975)

Burning rate 1.6 mm/min (CHRIS 1978; Ullmann 1975)

Upper flammability limit 16% (v/v) (NFPA 1978; Ullmann 1975)

Lower flammability limit 6.2% (v/v) (NFPA 1978)

Burning characteristics Burns with a smokey flame (Merck 1976)

Heat of combustion 1,134 kJ/mole (vapour) (CRC 1980)

Combustion products Carbon dioxide water and hydrogen chloride

and under certain conditions phosgene

(Ullmann 1975)

Flashback potential Vapour may travel considerable distance to a

source of ignition and flash back (NFPA 1978)

Vapour forms explosive mixtures with air Explosiveness (NFPA 1978) Electrical ignition hazard May be ignited by static discharge Other Properties Molecular weight of pure substance 98.96 (CRC 1980) Constituent components of typical 99.8% ethylene dichloride (Olin PDS 1980) commercial grade 99.5% ethylene dichloride (Dow MSDS 1980) Refractive index 1.4412 (25°C) (Ullmann 1975) 1.4448 (20°C) (CRC 1980) 0.887 mPa·s (15°C) (CRC 1980) Viscosity 0.82 mPa•s (20°C) (Ullmann 1975) 24.15 mN/m (20°C) (CRC 1980) Liquid interfacial tension with air 33.5 mN/m (20°C) (Ullmann 1975) 30 mN/m (25°C) (est.) (CHRIS 1978) Liquid interfacial tension with water Latent heat of fusion 8.75 kJ/mole (at melting point) (CRC 1980) Latent heat of sublimation 35.4 kJ/mole (25°C) (Lange's Handbook 1979; Ullmann 1975) Latent heat of vaporization 33.3 kJ/mole (at boiling point) (CRC 1980) Heat of formation -165.1 kJ/mole (25°C) (liquid) (Sussex 1977) -129.7 (gas) (25°C) Ionization potential 11.04 eV (Berman 1979) Heat capacity constant pressure (C_D) 135 J/(mole•°C) (25°C) (CRC 1980) 128.4 J/(mole•°C) (25°C) (ISH 1977) constant volume (C_v) 121 J/(mole•°C) (25°C) (CRC 1980; CHRIS 1978) Critical pressure 5,370 kPa (Lange's Handbook 1979) 5,570 kPa (Ullmann 1975) 288°C (Lange's Handbook 1979) Critical temperature 290°C (Ullmann 1975) 10.55 (20°C) (Ullmann 1975) Dielectric constant 9.0 x 106 ohms/cm (ISH 1977) Resistivity 1.161 x 10-3/°C (20°C) (Lange's Handbook Coefficient of thermal expansion 1979) (10-30°C) (Ullmann 1975) 0.14 W·m⁻¹·K⁻¹ (50°C) (Perry 1973) Thermal conductivity 0.136 W·m-1·K-1 (25°C) (Ullmann 1975) 350 g/m³ (20°C) (Verschueren 1977) Saturation concentration in air 537 g/m³ (30°C) (Verschueren 1977)

Corrosivity

In contact with water, corrodes iron and

certain other metals at elevated temperature

(MCA 1971)

Evaporation rate

2.4 g/($m^2 \cdot s$) (20°C) (this work)

Log10 octanol/water partition

1.48 (Hansch and Leo 1979)

coefficient

Solubility

In water

Of water in ethylene dichloride

In other common materials

Azeotropes

Vapour Weight to Volume Conversion Factor

0.873 g/100 mL (0°C) (Ullmann 1975)

0.8 g/100 mL (20°C) (Dow MSDS 1980) 0.895 g/100 mL (35°C) (Ullmann 1975)

0.16 g/100 mL (20°C) (ISH 1977)

Miscible in diethyl ether, very soluble in

ethanol, and soluble in acetone, benzene and

chloroform (CRC 1980)

With ethanol; 37% (w/w) ethanol, BP = 70.3°C

(Ullmann 1975)

With methanol; 32% (w/w) methanol, BP = 61°C (Ullmann 1975; ISH 1977)

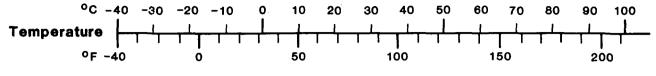
With water; 8.2% (w/w) water, BP = 70.5°C

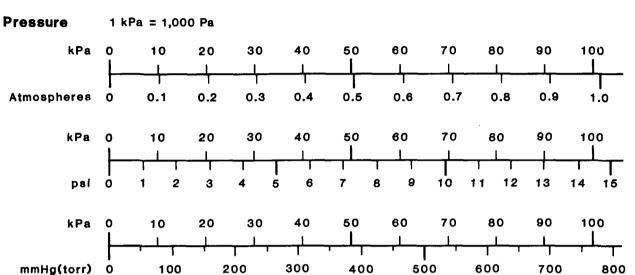
(Ullmann 1975; ISH 1977)

1 ppm = 4.115 mg/m^3 (20°C) (Verschueren 1977)

ETHYLENE DICHLORIDE

CONVERSION NOMOGRAMS





Viscosity

Dynamic

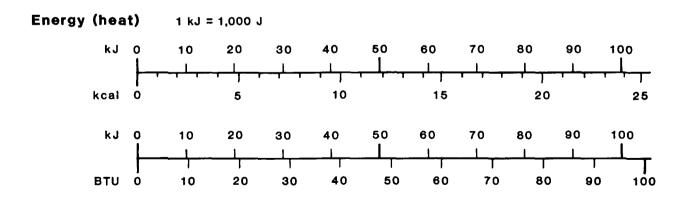
1 Pa-s = 1,000 centipoise (cP)

Kinematic

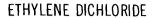
 $1 m^2/s = 1,000,000 centistokes (cSt)$

Concentration (in water)

1 ppm ≅ 1 mg/L







VAPOUR PRESSURE VS TEMPERATURE

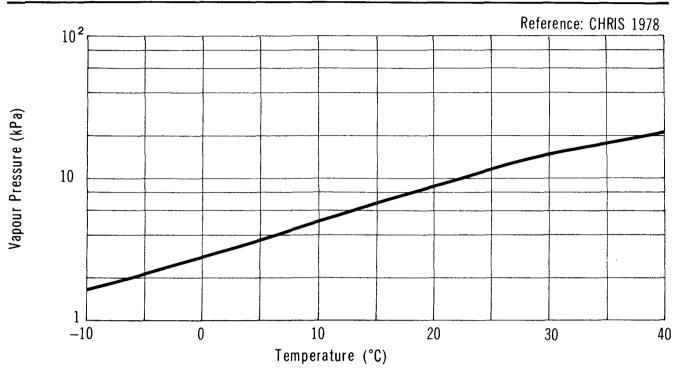
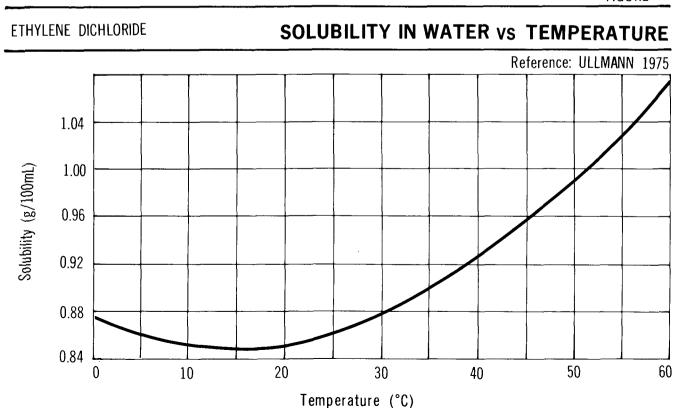


FIGURE 2



ETHYLENE DICHLORIDE

LIQUID DENSITY VS TEMPERATURE

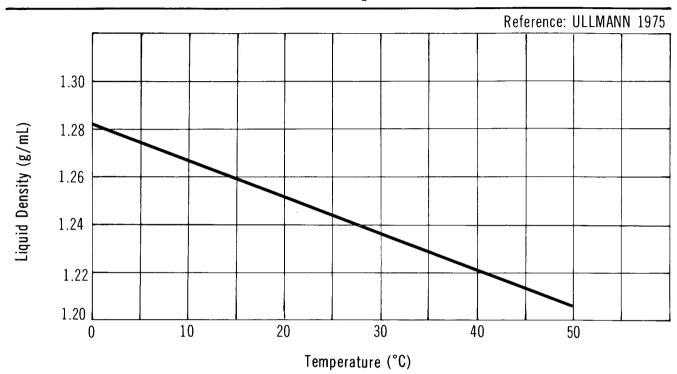
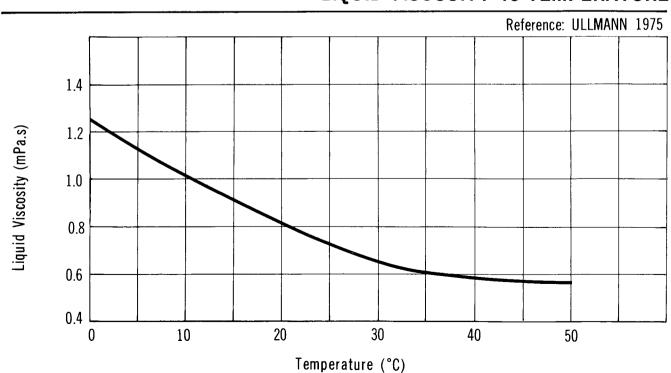


FIGURE 4

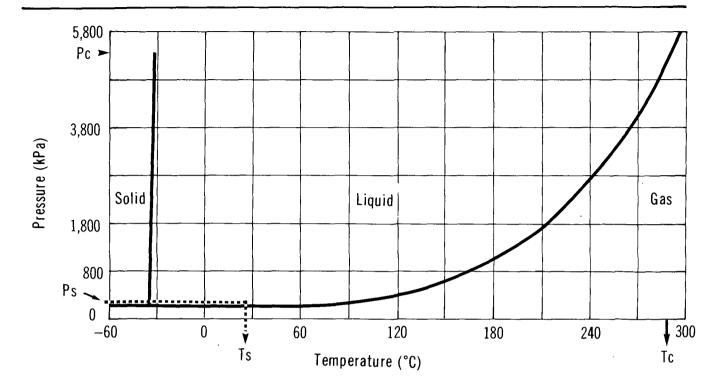
ETHYLENE DICHLORIDE

LIQUID VISCOSITY VS TEMPERATURE



ETHYLENE DICHLORIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Olin PDS 1980; Dow MSDS 1980)

Ethylene dichloride is sold in a commercial grade with a minimum purity of 99.5 or 99.8 percent.

3.2 Domestic Manufacturers (Corpus 1983; CBG 1980)

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

Dow Chemical Canada Inc. Box 1012, Modeland Road Sarnia, Ontario N7T 7K7 (519) 339-3131 Ethyl Canada Inc. 48 St. Clair Avenue West Toronto, Ontario M4V 1M7 (416) 962-1611

3.3 Major Transportation Routes (Corpus 1983)

Current Canadian production of ethylene dichloride is located primarily in Alberta at Fort Saskatchewan (78 percent of total production); and in Ontario, at Sarnia and Corunna (22 percent of total production). The product is usually shipped in bulk to users in the immediate area of production; thus, the major transportation routes are located in the Edmonton and Sarnia areas. In addition, a large portion of the Fort Saskatchewan production is exported to Japan and is transported to Vancouver by rail.

3.4 Production Levels (Corpus 1983)

| Company, Plant Location | | Nameplate Capacity kilotonnes/yr (1982) |
|--|--------------|--|
| Dow Chemical Canada, Sarnia, Ont. | | 165 |
| Dow Chemical Canada, Ft. Saskatchewan, | 630 | |
| Ethyl Canada, Corunna, Ont. | 9 | |
| | TOTAL | 804 |
| Domestic Production (1982) | 548 | |
| Imports (1982) | | |
| | TOTAL SUPPLY | 548 |

3.5 Manufacture of Ethylene Dichloride (FKC 1975)

- **3.5.1** Raw Materials. Raw materials used in the manufacture of ethylene dichloride are ethylene and chlorine or hydrogen chloride.
- **3.5.2 Manufacturing Process.** Ethylene dichloride, or 1,2-dichloroethane, may be produced by the catalytic chlorination of ethylene:

This is commonly done by mixing ethylene and chlorine in liquid ethylene dichloride. Where operated in conjunction with a hydrogen chloride source such as a vinyl chloride process, it is also made by oxychlorination of ethylene over a catalyst, in the vapour phase:

The ethylene dichloride product is washed, neutralized, and purified by fractionation. Other chlorinated hydrocarbons recovered may be recycled into other chlorinated solvent manufacture.

3.6 Future Development (Corpus 1983; CCPA 1982)

Dow Chemical Canada is planning to expand its ethylene dichloride plant in Fort Saskatchewan, Alberta, to a capacity of 816 kt/yr.

3.7 Major Uses in Canada (Corpus 1983; Olin PDS 1980)

Ethylene dichloride is used in the production of vinyl chloride monomer, in antiknock compounds in gasoline, and in the processing of adhesives and coatings.

3.8 Major Buyers in Canada (Corpus 1983; CBG 1980)

A & K PetroChem, Weston, Ontario
Basile Import/Export, St. Laurent, Quebec
Canada Colours & Chemicals Ltd., Toronto, Ontario
Ciscochem Inc., Brampton, Ontario
CPS Chemical Can. Ltd., Pointe Claire, Quebec
Dominion Cisco Industries Ltd., Weston, Ontario
Du Pont of Canada Ltd., Maitland, Ontario
General Intermediates of Canada, Edmonton, Alberta

Harrisons & Crosfield, Toronto, Ontario International Chem., Brampton, Ontario Kingsley & Keith, Toronto, Ontario

MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4

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

4.1.1.1 Railway tank cars. Railway tank cars used to transport ethylene dichloride are classified under the CTC/DOT Class 103, Class 104, Class 105A and Class IIIA tank specifications. Each specification is described in Table 2.

TABLE 2 RAILWAY TANK SPECIFICATIONS

| CTC/DOT* Specification Number | Description | |
|-------------------------------|--|--|
| 111A60W1 | Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi). | |
| 111A60F1 | Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi). | |
| 111A100W1 | Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Bottom outlet or washout optional. Test pressure 690 kPa (100 psi). | |
| 103W | Steel fusion-welded tank with dome. Uninsulated or insulated. 2% dome. Bottom outlet or washout optional. | |
| 104W | Same as 103W but must be insulated. | |
| 105A100W | Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement. Safety valve (518 kPA) (75 psi). Bottom outlet or washout prohibited. Test pressure 690 kPa 100 psi). | |

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

Ethylene dichloride is most commonly shipped in Class 111A60W1 railway tank cars with capacities of 75,700 L (16,700 Imp. gal.), 78,000 L (17,200 Imp. gal.), and 90,900 L (20,000 Imp. gal.). Figure 6 shows a typical IIIA60W1 railway car used to transport ethylene dichloride; Table 3 indicates railway tank car details associated with this drawing.

A safety relief valve set at 241 kPa (35 psi) and a safety vent set at 414 kPa (60 psi) are required on top of the rail car. A gauging device, either the rod type or the tape type, should be used. The top unloading connection must be protected by a housing. The maximum pressure allowable for the CTC/DOT 111A100W1 rail cars is 448 kPa (65 psi). When the 111A60W1 or 111A60F1 cars are used, this maximum pressure would be 276 kPa (40 psi).

4.1.1.2 Tank motor vehicles. Ethylene dichloride is transported by tank motor vehicles with tanks classed as non-pressure vessels under the Transport Canada Specification TC306. Pressure for such tanks must not exceed 101 kPa (15 psi). Specification TC307 incorporating MC304 may also be used. This is a pressure vessel with tank designed and constructed under the ASME Code. Motor vehicle tanks are similar to the railway tanks previously described. These highway tankers are usually unloaded by pump from the top unloading connection valve (MCA 1971).

The off-loading equipment and procedures for tank motor vehicles are similar to those for railway tank cars, to be discussed later.

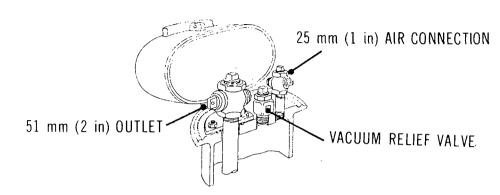
4.1.2 Packaging. In addition to railway bulk shipments, ethylene dichloride is also transported in drums. Drums fabricated from a variety of construction materials are permitted (TDGC 1980). Aluminum drums are not recommended and are not frequently used (CCPA 1982; Olin PDS 1980). Table 4 describes drums for ethylene dichloride service.

4.2 Off-loading

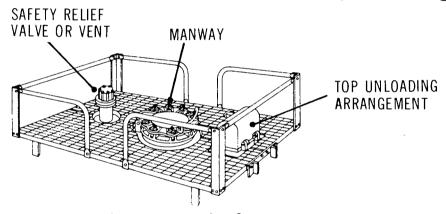
- 4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken:
- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution signs displayed.

RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979, RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

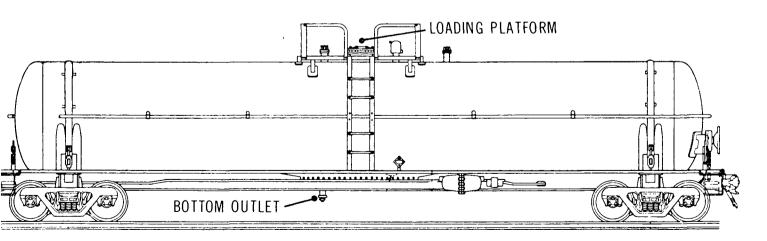


Illustration of tank car layout

| | Tank Car Size (Imp. Gal.) | | | | | |
|---|---|--|---|--|---|--|
| Description | 16,700 | | 17,200 | | 20,000 | |
| Overall | | | | | | |
| Nominal capacity Car weight - empty Car weight - (max.) | 75,700 L 33,900 kg 119,000 kg | (16,700 gal.) (74,700 lb.) (263,000 lb.) | 78,000 L 33,900 kg 83,500 kg | (17,200 gal.) (74,700 lb.) (184,000 lb.) | 90,900 L (20, 38,900 kg (8, 119,000 kg (2 | 5,800 lb.) |
| <u>Tank</u> | | | | | | |
| Material Thickness Inside diameter Test pressure Burst pressure | Steel 11.1 mm 2.60 m 414 kPa 1,640 kPa | (7/16 in.) (102 in.) (60 psi) (240 psi) | Steel 11.1 mm 2.62 m 414 kPa 1,640 kPa | (7/16 in.) (103 in.) (60 psi) (240 psi) | Steel 11.1 mm 2.74 414 kPa 1,640 kPa | (7/16 in.) (108 in.) (60 psi) (240 psi) |
| Approximate Dimensions | | | | | | |
| Coupled length Length over strikers Length of truck centres Height to top of grating Overall height Overall width (over grabs) Length of grating Width of grating | 17 m 16 m 13 m 4 m 5 m 3.2 m 2-3 m 1.5-2 m | (57 ft.) (53 ft.) (42 ft.) (12 ft.) (15 ft.) (127 in.) (8-10 ft.) (5-6 ft.) | 17 m 16 m 13 m 4 m 5 m 3.2 m 2-3 m 1.5-2 m | (57 ft.) (53 ft.) (42 ft.) (12 ft.) (15 ft.) (127 in.) (8-10 ft.) (5-6 ft.) | 18 m 17 m 14 m 4 m 5 m 3.2 m 2-3 m 1.5-2 m | (60 ft.) (57 ft.) (45 ft.) (13 ft.) (15 ft.) (127 in.) (8-10 ft.) (5-6 ft.) |
| Loading/Unloading Fixtures | | , | | | | |
| Top Unloading | | | | | | |
| Unloading connection Manway/fill hole Air connection | 51 mm 203-356 mr 25-51 mm | (2 in.) n (8-14 in.) (1-2 in.) | 51 mm 203-356 mn 25-51 mm | (2 in.) n (8-14 in.) (1-2 in.) | 51 mm 203-356 mm 25-51 mm | (2 in.) (8-14 in.) (1-2 in.) |
| Bottom Unloading | | | | | | |
| Bottom outlet | 102-152 mr | n (4-6 in.) | 102-152 mm | n (4-6 in .) | 102-152 mm | (4-6 in.) |
| Safety Devices | Safety vent | or valve | Safety vent | or valve | Safety vent | or valve |
| <u>Dome</u> | None | | None | | None | |
| Insulation | Optional | | Optional | | Optional | |

TABLE 4 DRUMS

| Type of Drum | Designation | Description | Figure No. (If Any) |
|--|-------------|---|------------------------|
| Steel | 1A1 | Nonremovable head, reusable | 7 |
| | 1A1A | 1A1 with reinforced chime | 7 |
| | 1A1B | IA1 with welded closure flange | 7 |
| | 1A1D | IA1 with coating (other than lead) | 7 |
| | 1A2 | Removable head, reusable | 7 |
| | 1A3 | Nonremovable head, single use only | 7 |
| Monel* | TC5M | | 7 |
| Aluminum | 1B1 | Nonremovable head | |
| | 1B2 | Removable head | |
| Steel drums with inner plastic receptacle | 6HA1 | Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity of 225 L (49 gal.) | |
| Fibreboard drums with inner plastic receptacle | 6HG1 | Outer container of convolutely wound plies of fibreboard. Inner plastic receptacle. Maximum capacity of 225 L (49 gal.) | |

^{*} See section 4.3 of this report.

- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- Effectively ground the tank car.

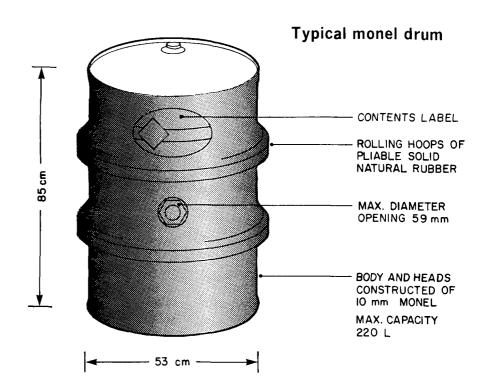
Two means of off-loading are used for these rail cars, top off-loading and bottom off-loading. Proceed with top off-loading as follows (MCA 1971):

- After removing the protective housing from the discharge line at top of car, connect the 51 mm (2 in.) unloading line.
- Off-load the tanker by pump only.

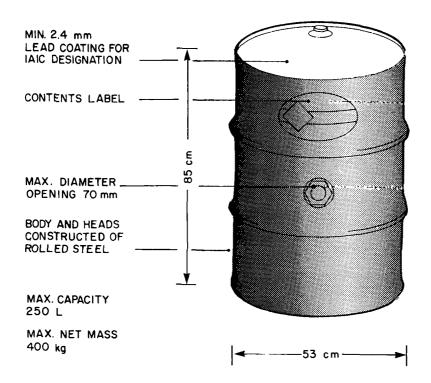
Proceed with bottom off-loading in the following manner using gravity flow:

- Note: bottom unloading is almost never practiced in Canada (CCPA 1982).
- After connecting the unloading line to a 152 mm (6 in.) bottom outlet, open the inside bottom valve by turning the valve rod handle at the top of the car.
- Off-load the car by gravity.

TYPICAL DRUM CONTAINERS



Typical steel drum



4.2.2 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in ethylene dichloride service. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets and pumps.

Schedule 40 seamless ASTM Al06 carbon steel pipes and fittings lined with chlorinated polyether resins are recommended for ethylene dichloride lines (DCRG 1978). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak after a very short time. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipeline should be tested with air at pressures from 345 to 518 kPa (50 to 75 psi) and all leaks carefully stopped. If leaks develop in service, the only satisfactory way to repair them is to chip out the bad weld and reweld, or to replace the section of pipe.

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

Flexible bellows-type expansion joints should be used for the flexible sections of the unloading line. They are manufactured with ASA ductile iron flanges with expansion members molded from tetrafluoroethylene resin (Dow PPS 1972). Stainless steel hose should be used in places where flexible bellows-type expansion joints are used for the flexible sections of the unloading line (CCPA 1982).

For valving, cast iron or cast steel diaphragm valves lined with chlorinated polyether or polyvinylidene chloride resin will serve adequately (DPLV 1972).

Viton, asbestos and Teflon gasket material may be used at normal temperature ranges (CCPA 1982).

A single-suction, sealless magnetic drive centrifugal pump with "wet end" material of 316 stainless steel gives good results. There is virtually no leakage from this type of pump. Provision must be made for draining the pump so that repairs can be made safely. The pump should be equipped with flanges at both suction and discharge openings; screw connections are subject to leakage and should be avoided.

4.3 Compatibility with Materials of Construction

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

Recommended:

This material will perform satisfactorily in the given application.

Conditional:

Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended:

Material will be severely affected in this application and should not

be used.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

| | Chemical | | Material of Construction | | |
|-----------------------|----------|---|--|-------------|---|
| | CHemic | a1 | | | Not |
| Application | Conc. | Temp. (°C) | Recommended C | Conditional | Recommended |
| I. Pipes and Fittings | 1 99.5% | 23 | Carbon Steel - seamless ASTM A106 lined with Chlorinated Polyether Resin (DCRG 1970) SS316 (JSSV 1979) | | PVC I PVC II (DPPED 1967) |
| | | To operat- ing limit of mate- rial | PE (MWPP 1978) | | |
| | | | | | Chlorinated Polyether (DCRG 1978) |
| | | 24 | PP PVDC (DCRG 1978) | | |
| | | 135 | PVDF (DCRG 1978) | | |
| 2. Valves | 99.5% | 21 | SS 316 (JSSV 1979) | | |
| 3. Pumps | | Cold | All Bronze SS 304 SS 316 Monel (HIS 1969) | | |
| 4. Others | | 22 | | | PVC CPVC (TPS 1978) |
| | | 66 | PP (TPS 1978) | | |

| | Chemical | | Material of Construction | | |
|-------------|----------|------------|--------------------------|-------------------|-------------------------------------|
| Application | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | | | | IIR EPDM (GPP) | NR SBR CR NBR CSM (GPP) |
| | To 100% | 24-100 | Glass (CDS 1967) | | |
| | 100% | 24 | Wood (CDS 1967) | | Concrete (CDS 1967) |

TABLE 6

MATERIALS OF CONSTRUCTION

| Abbreviation | Material of Construction |
|--------------------------------|--|
| | Aluminum |
| | Bronze |
| | Carbon Steel |
| | Chlorinated Polyether |
| CPVC | Chlorinated Polyvinyl Chloride |
| CR | Polychloroprene (Neoprene) |
| CSM | Chlorosulphonated Polyethylene (Hypalon) |
| EPDM | Ethylene Propylene Rubber |
| | Fluorine Rubber (Viton) |
| | Glass |
| IIR | Isobutylene/Isoprene (Butyl) Rubber |
| NBR | Acrylonitrile/Butadiene Rubber (Nitrile, Buna N) |
| NR | Natural Rubber |
| | Nickel-Copper Alloy (Monel) |
| PE | Polyethylene |
| pp | Polypropylene |
| PVC (followed by grade if any) | Polyvinyl Chloride |
| PVDC | Polyvinylidene Chloride |
| | |

| Abbreviation | Material of Construction |
|------------------------|----------------------------------|
| PVDF | Polyvinylidene Fluoride |
| SBR | Styrene/Butadiene (GR-5, Buna S) |
| SS (followed by grade) | Stainless Steel |
| | Wood |

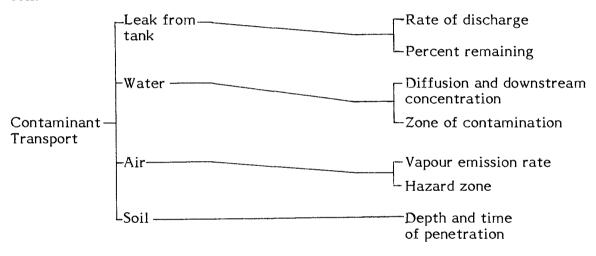
5 CONTAMINANT TRANSPORT

5.1 General Summary

Ethylene dichloride is commonly transported in tank cars. When spilled in water, it will sink and dissolve very slowly. When spilled on soil, the liquid will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may cause environmental problems.

Since ethylene dichloride is moderately volatile, the irritating vapour released from a liquid pool on the ground surface is a potential environmental hazard.

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



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. Thus, assumptions may vary for ethylene dichloride for each medium studied. However, the assumptions made for each medium are consistent throughout the EnviroTIPS series, allowing comparison of the behaviours of different chemicals.

5.2 Leak Nomograms

5.2.1 Introduction. Ethylene dichloride is commonly transported in railway tank cars as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size has been chosen for development of the leak nomograms. It is

approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80,000 L. This size has been used throughout the EnviroTIPS series so that comparisons of behaviour can be made.

If a tank car loaded with ethylene dichloride is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the discharge rate of the liquid. Because of the relatively low volatility of ethylene dichloride and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

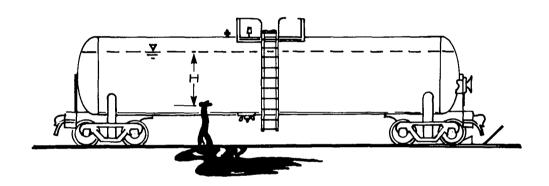


FIGURE 8 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

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

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

5.2.2 Nomograms.

5.2.2.1 Figure 9: Percent remaining versus time. Figure 9 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

ETHYLENE DICHLORIDE

PERCENT REMAINING VS TIME

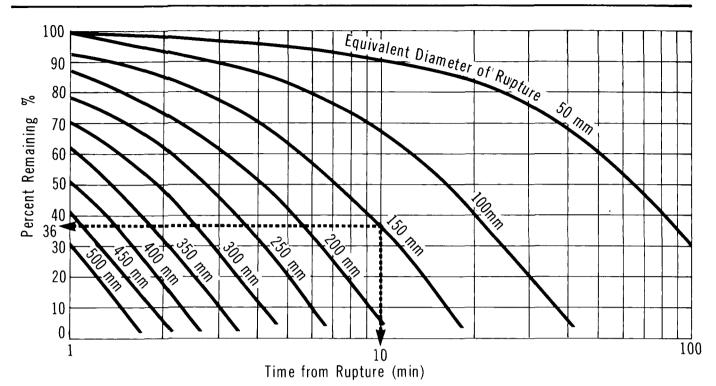
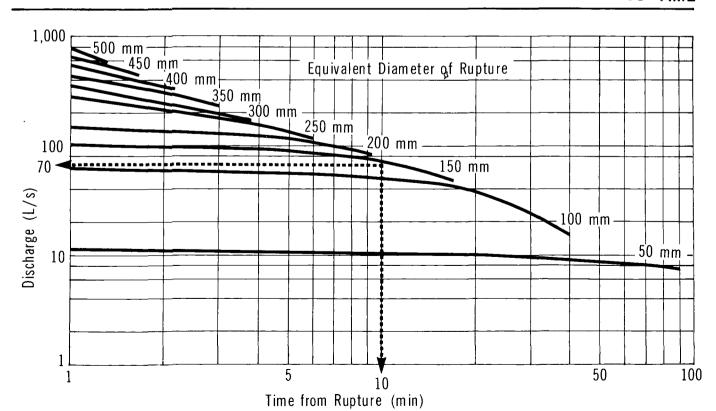


FIGURE 10

DISCHARGE RATE VS TIME



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

5.2.2.2 Figure 10: Discharge rate versus time. Figure 10 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture, for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80,000 L.

5.2.3 Sample Calculations.

i) Problem A

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

Solution to Problem A

- Use Figure 9
- . With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28,800 L

ii) Problem B

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

Solution to Problem B

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

5.3 Dispersion in the Air

5.3.1 Introduction. Since ethylene dichloride is a moderately volatile liquid, direct venting of the vapour to the atmosphere from a hole in a punctured vessel does not constitute a significant hazard downwind. Only vapour released from a liquid pool spilled on a ground or water surface is treated here. The increased surface area from such a spill would increase evaporation and thus pose a hazard downwind.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based

on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 11 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source as a virtual point source (with the same vapour emission rate, Q) located 10 equivalent pool radii upwind.

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

Figure 13: vapour emission rate from a liquid pool as a function of maximum pool

Figure 7: weather conditions

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

Table 8: maximum plume hazard half-widths

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

and wind speed

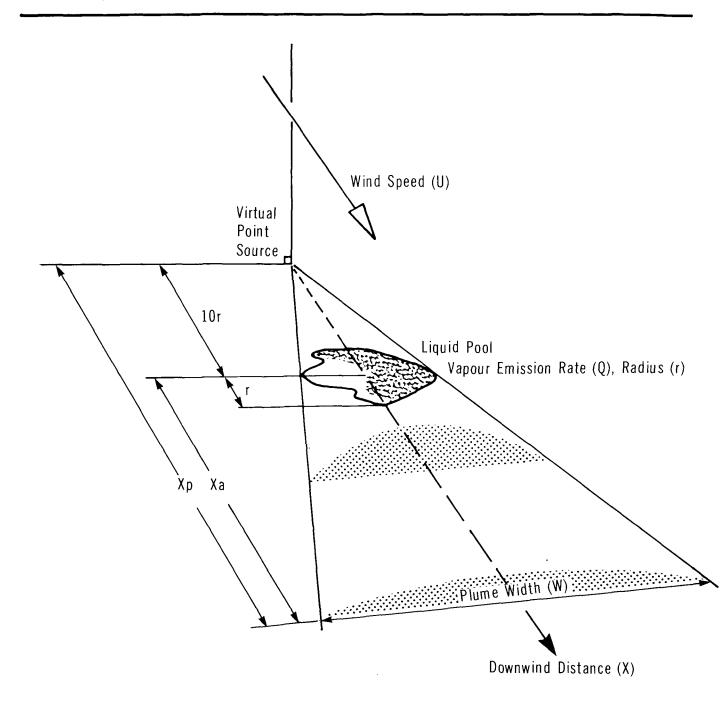
Figure 20: maximum spill radius as a function of spill size

The flow chart given in Figure 12 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" and "equivalent pool radius" are contained in Sections 5.2 and 5.4, respectively. A description of each vapour dispersion nomogram and its use follows.

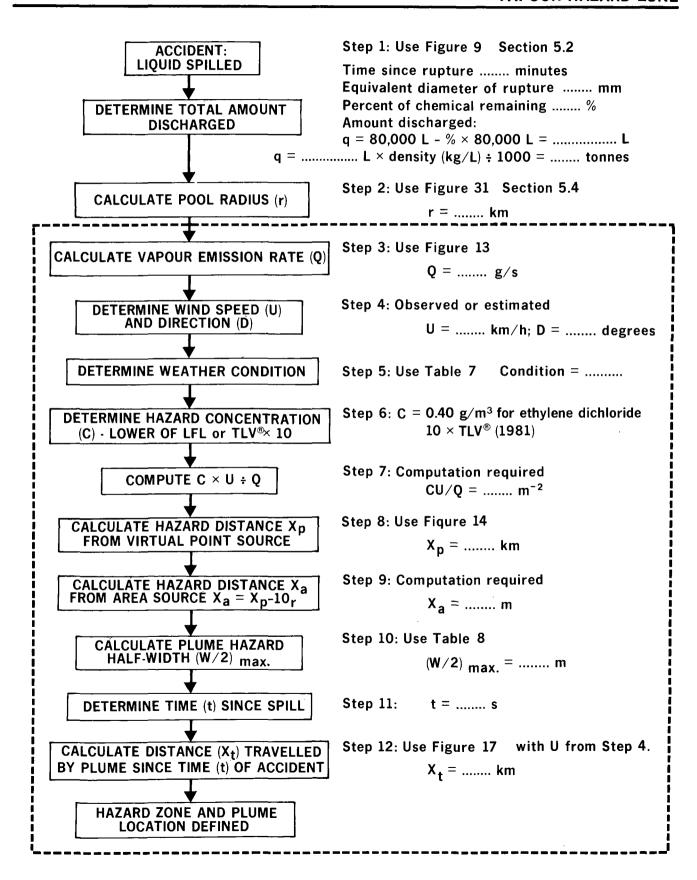
5.3.2.1 Figure 13: Vapour emission rate versus liquid pool radius for various temperature. An evaporation rate for ethylene dichloride has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for ethylene dichloride at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 2.4 g/(m²·s). Evaporation rates at other temperatures have been calculated using the evaporation rate equation, which, at a given wind speed, is dependent on ambient temperature and the vapour pressure (Perry 1973) of ethylene dichloride at that temperature. For example, evaporation rates of 0.90 g/(m²·s) at 0°C and 3.62 g/(m²·s) at 30°C were calculated for a wind speed of 4.5 m/s.

Using Figure 20, the maximum spill radius corresponding to various spill amounts of ethylene dichloride may be determined. The resultant spill areas and the

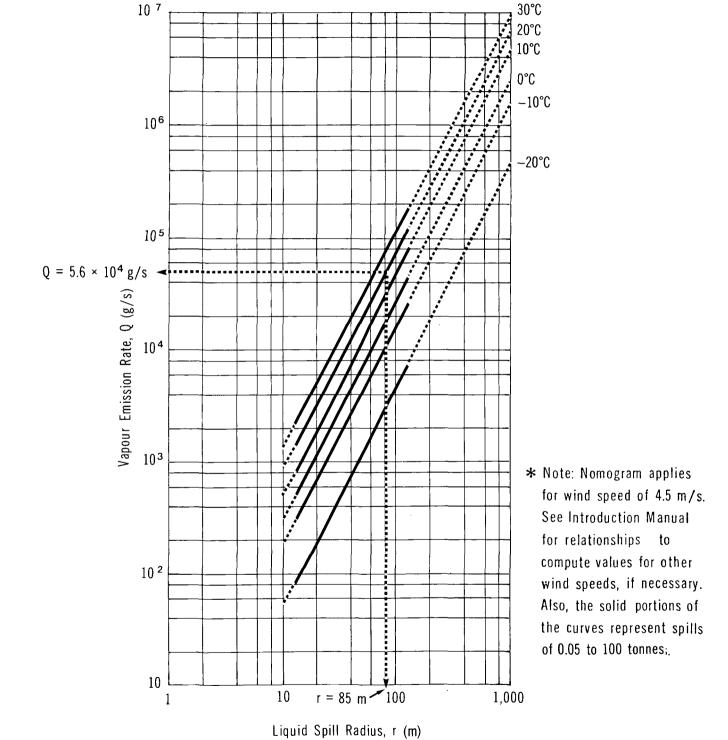
SCHEMATIC OF CONTAMINANT PLUME



FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE



VAPOUR EMISSION RATE VS LIQUID SPILL RADIUS FOR VARIOUS TEMPERATURES *



ethylene dichloride evaporation rates provide the basis for preparation of the vapour release rate versus spill radius nomogram in Figure 13.

Use: For a pool of ethylene dichloride of known radius, the rate (Q) at which ethylene dichloride vapour is released to the atmosphere at a given temperature can then be estimated from Figure 13. The solid portion of the curves represents spills of 0.05 to 100 tonnes, the latter representing about one standard 80,000 L rail car load of ethylene dichloride. It should be noted that Figure 13 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of ethylene dichloride vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

It should also be noted that the determination of the evaporation rate is based on the spill radius on calm water (Table VI, CHRIS 1974). The spill radius employed was that of benzene, since the vapour pressure of ethylene dichloride is similar to that of benzene (the fact that ethylene dichloride is heavier than water is neglected since this property is not under consideration here). Since calm water represents a flat, unbounded surface compared to the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous), the spill radius on calm water is considered to provide the maximum value. Therefore, when spills on land are assessed by using the water algorithm, the spill radius would be overestimated and worst case values are provided. Figure 20 provides estimates of these values.

5.3.2.2 Figure 14: Vapour concentration versus downwind distance. Figure 14 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 14, the weather condition must be determined from Table 7.

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

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

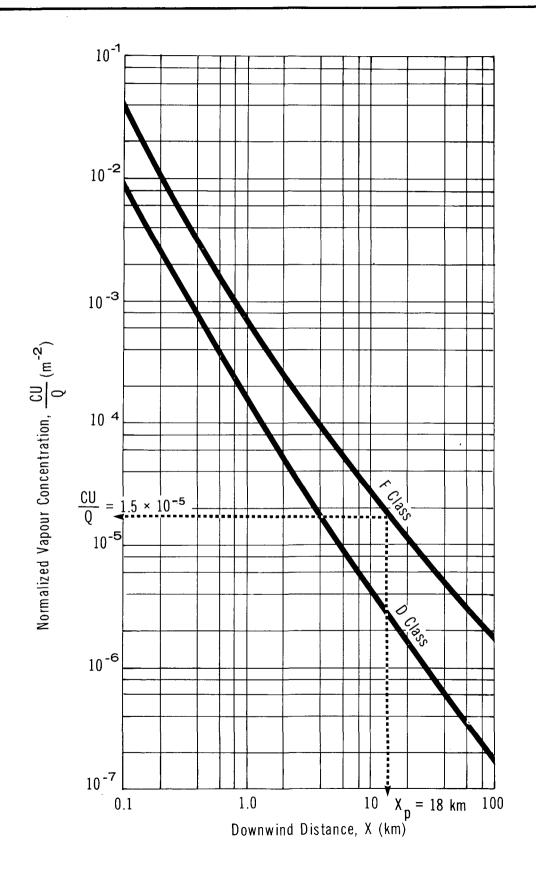


TABLE 7 WEATHER CONDITIONS

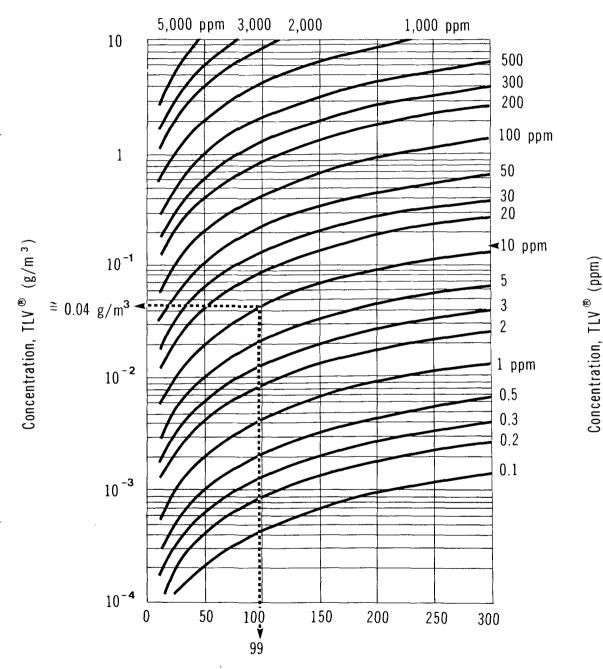
| Weather Condition F | Weather Condition D | | |
|---|-------------------------------|--|--|
| Wind speed < 11 km/h (~3 m/s) and one of the following: | Most other weather conditions | | |
| - overcast day | | | |
| - night time | | | |
| - severe temperature inversion | | | |

the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value (TLV*, in g/m^3), or the Lower Flammability Limit (LFL in g/m^3). Note: To convert the TLV* (in ppm) and the LFL (in % by volume) to concentrations in g/m^3 , use Figures 15 and 16

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

5.3.2.3 Table 8: Maximum plume hazard half-widths. This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$, for a range of Q/U values under conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the ethylene dichloride Threshold Limit Value (TLV°) of 0.04 g/m^3 , or 0.40 g/m^3 . The maximum plume hazard half-width represents the maximum half-width of the ethylene dichloride vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV°. Table 8 is therefore only applicable for an ethylene dichloride hazard concentration limit of $10 \times TLV$ °, or 0.40 g/m^3 . Also, data are provided up to a maximum hazard distance downwind of 100 km.

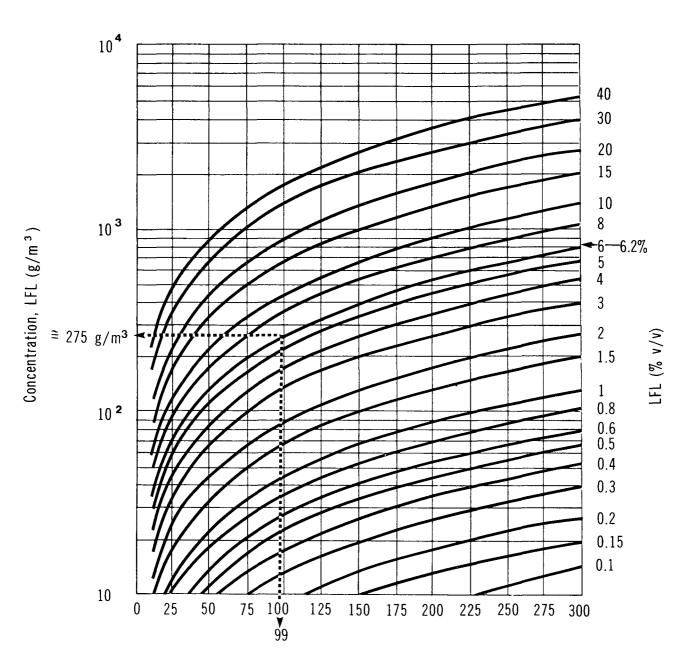
Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 15,000 to 2,500,000 g/s, corresponding to ethylene dichloride spills in the range of about 3 to 5,500 tonnes, respectively. If the entire contents of an 80,000 L (17,600 Imp. gal.) tank car spills, the mass spilled would be



Molecular Weight

Example: Ethylene Dichloride, MW = 99, TLV® = 10 ppm, then TLV® in $g/m^3 \cong 0.04$

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



Molecular Weight Example: Ethylene Dichloride, MW = 99, LFL = 6.2%, then LFL in g/m³ \cong 275

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

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

| Weather Condition D | | | Weather Condition F | | F |
|---------------------|-----------------------------|----------------|---|------------------------------------|---|
| Q/U (g/m) | (W/2) _{max} (m) | K | Q/U (g/m) | (W/2) _{ma} (m) | ax |
| 2,500,000 | 3,195 | (Xp <99.5 km)* | 250,000 | 1,475 | (Xp <99.5 km) * |
| 2,000,000 | 2,785 | | 200,000 | 1,250 | |
| 1,500,000 | 2,330 | | 150,000 | 1,010 | |
| 1,000,000 | 1,815 | | 100,000 | 745 | |
| 750,000 | 1,520 | | 75,000 | 600 | |
| 500,000 | 1,180 | | 50,000 | 445 | |
| 250,000 | 770 | Q/U = 26,670 → | 25,000 | 275 | $\rightarrow (W/2)_{max} = 285 \text{ m}$ |
| 200,000 | 670 | | 20,000 | 240 | |
| 100,000 | 450 | | 10,000 | 155 | |
| 75,000 | 380 | | 7,500 | 130 | |
| 50,000 | 300 | | 5,000 | 100 | |
| 25,000 | 200 | | 2,500 | 65 | |
| 20,000 | 175 | | 1,000 | 40 | |
| 15,000 | 150 | | 500 | 25 | |
| 10,000 | 115 | | 250 | 20 | |
| 7,500 | 100 | | | | |
| 5,000 | 80 | | | | |
| 2,500 | 55 | | | | |
| 1,000 | 35 | | | *Data are provided up to a miximum | |
| 500 | 25 | | downwind hazard distance (X _p) of 99.5 km | | |

Example: A spill releasing ethylene dichloride vapour at the rate of $Q = 5.6 \times 10^4$ g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 26,670 g/m which results in a maximum plume hazard half-width $(W/2)_{max} = 285$ m.

Note: Above table is valid only for an ethylene dichloride concentration of $10 \times TLV^{\circ}$, or 0.40 g/m³.

100,000 kg or approximately 100 tonnes. Therefore, under Class D of Table 8, data are provided for up to 55 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 750 to 250,000 g/s, corresponding to ethylene dichloride spills in the range of about 0.05 to 500 tonnes, respectively. Therefore, under Class F of Table 8, data are provided for up to 5 times a standard rail car load.

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

5.3.2.4 Figure 17: Plume travel time versus travel distance. Figure 17 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship X_t = Ut for a range of typical wind speeds.

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

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

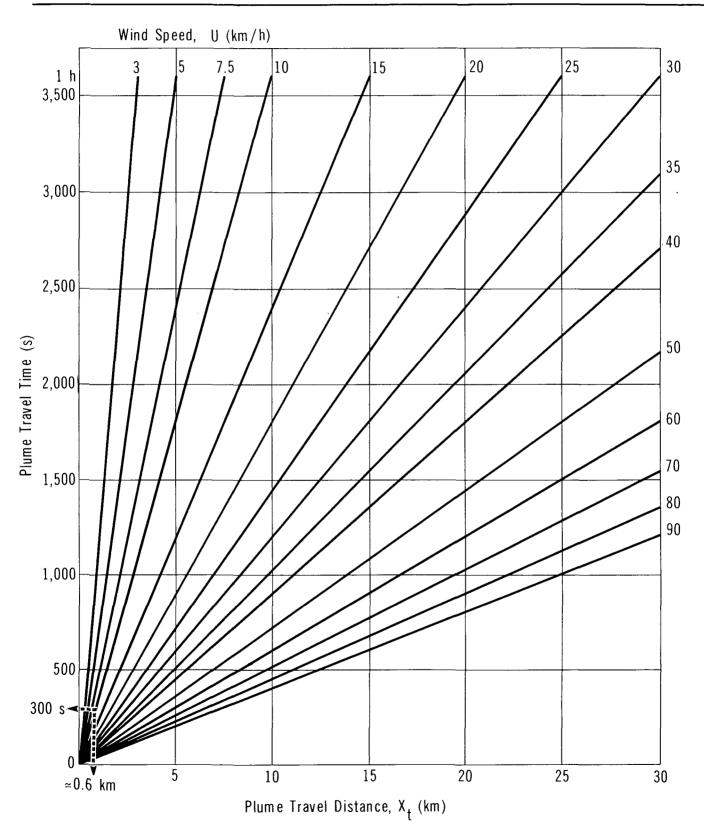
Problem:

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

Solution

Step 1: Quantity spilled is given, 20 tonnes

PLUME TRAVEL TIME VS TRAVEL DISTANCE



- Step 2: Determine pool radius (r) for spill of 20 tonnes
 - . Use observed (measured) pool radius if possible. If not, use the maximum radius from Figure 20. Note that use of these data, which apply specifically to spills on water, will result in an exaggerated pool radius on land
 - Radius (r) = 85 m or 0.085 km
- Step 3: Calculate vapour emission rate (Q) at T = 20°C
 - From Figure 13, for r = 85 m and T = 20°C, $Q = 5.6 \times 10^4$ g/s
- Step 4: Determine wind speed (U) and direction (D)
 - . Use available weather information, preferably on-site observations
 - . Given:

U = 7.5 km/h, then $U = 7.5 \div 3.6 = 2.1 \text{ m/s}$

D = NW or 315° (D = Direction from which wind is blowing)

- Step 5: Determine weather condition
 - From Table 7, weather condition = F since U is less than 11 km/h and it is night
- Step 6: Determine hazard concentration limit (C)
 - . This is the lower of 10 times the TLV®, or the LFL, so for ethylene dichloride

$$C = 0.40 \text{ g/m}^3 \text{ (TLV} = 0.04 \text{ g/m}^3; \text{ LFL} = 275 \text{ g/m}^3)$$

Step 7: Compute CU/Q

CU/Q =
$$\frac{0.40 \times 2.1}{5.6 \times 10^{4}} = 1.5 \times 10^{-5} \text{ m}^{-2}$$

- Step 8: Calculate downwind distance (X_D) from the virtual point source
 - From Figure 14 with CU/Q = 1.5 x 10^{-5} m⁻² and weather condition F, $X_D \simeq 18$ km
- Step 9: Calculate hazard distance (Xa) downwind of the area source

. With
$$X_p = 18$$
 km and $r = 0.085$ km then $X_a = X_p - 10r = 18$ km - 10 (0.085 km) = 17.2 km

- Step 10: Calculate plume hazard half-width (W/2)_{max}
 - . Use Table 8
 - . With Q = 5.6×10^4 g/s and U = 2.1 m/s 5.6×10^4 then Q/U = $\frac{5.6 \times 10^4}{2.1}$ = 26,670 g/m

- . Then for weather condition F the closest Q/U value is between 25,000 and 50,000 g/m, which gives $(W/2)_{max} \approx 285 \text{ m}$
- Step 11: Determine the time, in seconds, since spill
 - $t = 5 \min x 60 = 300 s$
- Step 12: Calculate distance travelled (X_t) by vapour plume since time of accident
 - Using Figure 17 with t = 300 s and U = 7.5 km/h, then $X_t = 0.6$ km (more accurately from Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 13: Map the hazard zone

- . This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (285 m) by the hazard distance downwind of the area source (17.2 km) along the direction of the wind, as shown in Figure 18
- If the wind is reported to be fluctuating by 20° about 315° (or from $315^{\circ} \pm 10^{\circ}$), the hazard zone is defined as shown in Figure 19
- Note that the plume has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 133 minutes before the plume reaches the maximum downwind hazard distance of 17.2 km

5.4 Behaviour in Water

5.4.1 Introduction. Ethylene dichloride sinks and dissolves very slowly in water. Nomograms have been prepared to estimate the length and width of the zone of contamination in a non-tidal river assuming no dissolution occurs (Figure 20) and to estimate the maximum downstream concentration assuming the entire spill is dissolved. These represent the two worst case scenarios for the extent of the zone of contamination and the downstream pollutant concentration for a spill of ethylene dichloride.

To estimate the zone of contamination on a river bed resulting from a spill of an insoluble, high density liquid on water, the terminal fall velocities (V_t) of the discrete particles have been estimated using a mathematical model (Thibodeaux 1980). The fall velocity of an individual particle is a function of its specific gravity, size, and cross-sectional area, together with the density and viscosity of water. The drag force, tending to resist fall of the particle through water, varies for different flow regimes.

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

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

Wind $U = 7.5 \text{ km/h from } 315^{\circ} \text{ (NW)}$

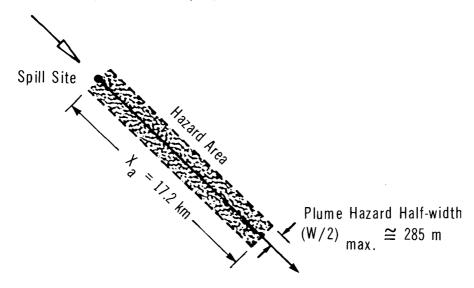
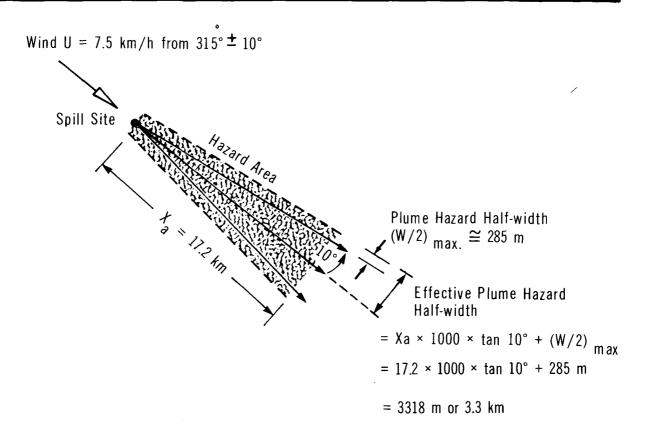


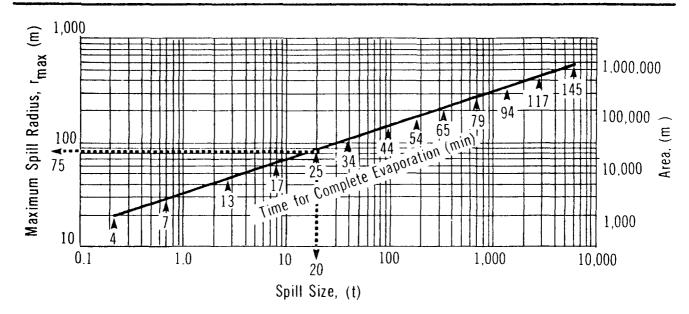
FIGURE 19

ETHYLENE DICHLORIDE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM



MAXIMUM SPILL RADIUS VS SPILL SIZE



maximize the estimated spill length and width. Details of the model are outlined in the Introduction Manual.

As ethylene dichloride dissolves in water, mixing takes place and the spill is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence, while in calm water mixing takes place by molecular diffusion. It should be noted that in preparing nomograms, total dissolution will be assumed so as to represent a worst case value, although historical experience has shown that in some situations little mixing actually occurs.

To estimate pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The model employed is strictly applicable to neutrally buoyant liquids and solids that dissolve in water. Application of this model to ethylene dichloride will produce a worst case scenario as noted above.

The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 (W/d <100) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

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

5.4.2 Nomograms.

- 5.4.2.1 Zone of streambed contamination no dissolution. The following nomograms are presented to calculate the length and width of the zone of contamination on the bed of a non-tidal river and in still water.
- Figure 21: fall velocity versus equivalent diameter of puncture for a range of average stream velocities
- Figure 22: settling time versus terminal fall velocity for a range of stream velocities
- Figure 23: downstream distance versus settling time for a range of average stream velocities
- Figure 24: spill width versus equivalent diameter of puncture for a range of stream depths

Figure 21: Fall velocity versus puncture size. The size of the smallest droplets is a function of the hole size, the physical characteristics of the chemical and of water, and the relative velocity with which the chemical impacts the water. For development of the nomogram, the exit velocity from the tank car was taken as the vertical component of velocity when the fluid jet hits the water surface. Figure 21 provides an estimate of the terminal fall velocity in water of the smallest droplets of ethylene dichloride as a function of the diameter of the puncture and the average stream velocity. For stream velocities less than 1 m/s, the curve for 1 m/s may be used as a reasonable approximation. Turbulent mixing in a stream would slow the fall time of the droplets - especially the smaller ones. This effect is not included in this manual.

Figure 22: Settling time versus terminal fall velocity. Based on a fall velocity (V_t) determined from Figure 21, the time (t) for the smallest droplets to settle to the bottom of a river of depth (d), neglecting turbulent mixing effects, can be estimated from Figure 22.

Figure 23: Distance versus settling time. Based on the settling time derived from Figure 22, the downstream distance (X) at which the smallest droplets of ethylene dichloride will reach the river bed can be determined from Figure 23, for a range of average stream velocities.

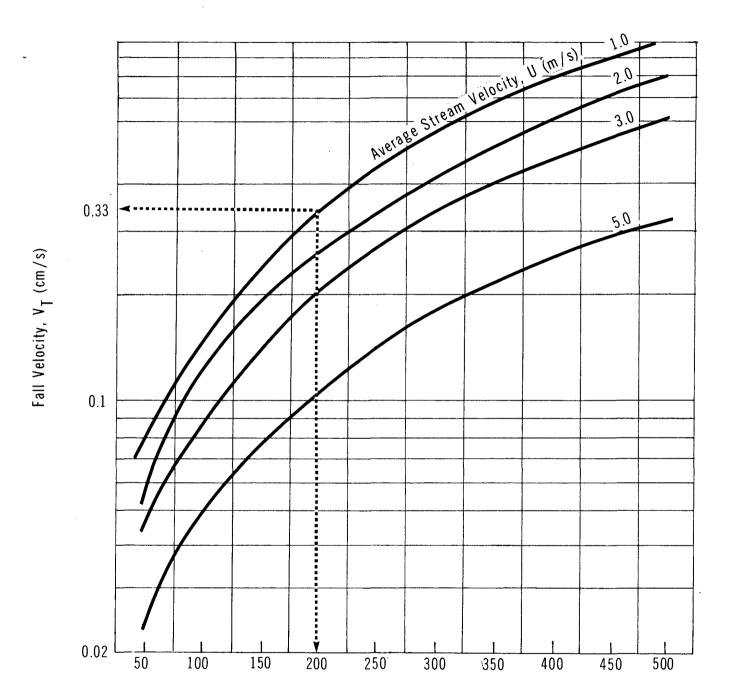
Figure 24: Spill width versus puncture size. For a given size of puncture, the width (W) of the zone of contamination on the streambed can be established from Figure 24 for a range of stream depths. Again, the nomogram indicates a maximum spill width based on the spread of the smallest droplet sizes. The spill width (W) also provides an estimate of the diameter of the zone of contamination for spills on a still water body.

5.4.2.2 Downstream pollutant concentration - total dissolution. The following nomograms are presented to calculate pollutant concentration in non-tidal rivers and in lakes (still water):

Non-tidal Rivers

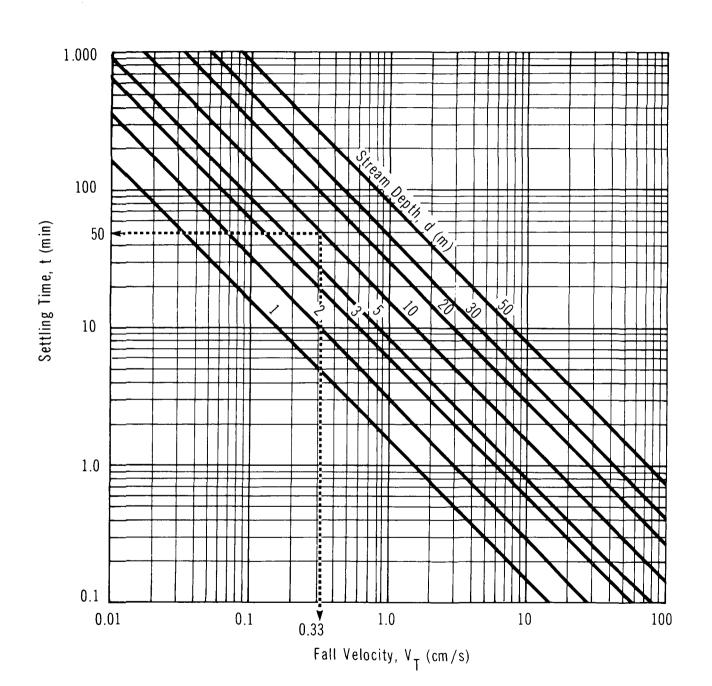
| Figure 26: | time versus distance for a range of average stream velocities | | | |
|------------|---|--|--|--|
| Figure 27: | hydraulic radius versus channel width for a range of stream depths | | | |
| Figure 28: | diffusion coefficient versus hydraulic radius for a range of average stream velocities $% \left(1\right) =\left(1\right) \left(1\right) \left$ | | | |
| Figure 29: | alpha* versus diffusion coefficient for various time intervals | | | |

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

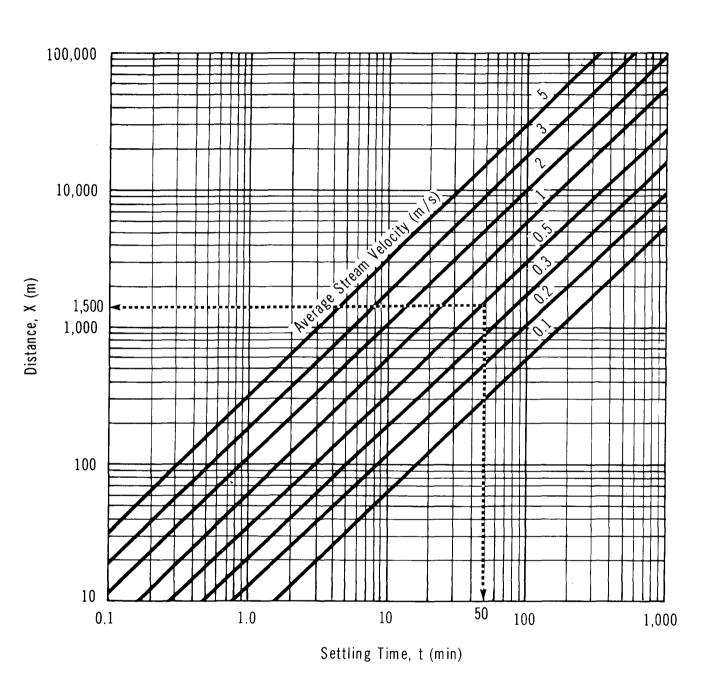


Equivalent Diameter of Puncture, d (mm)

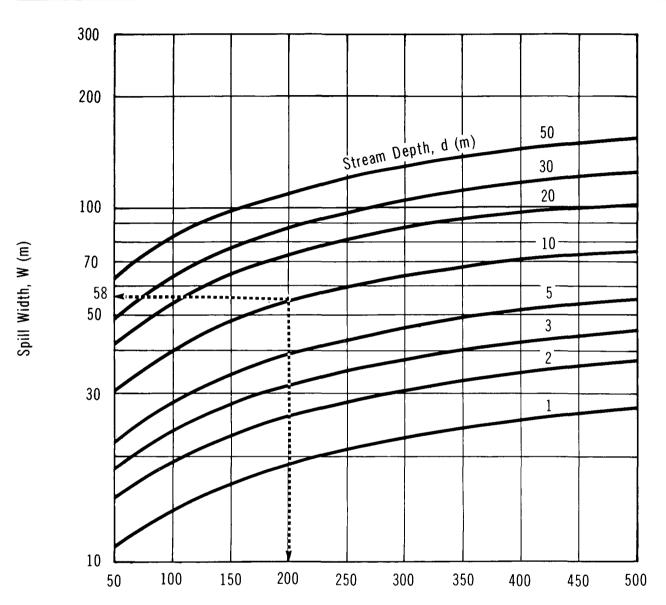
SETTLING TIME VS FALL VELOCITY



DISTANCE VS SETTLING TIME



SPILL WIDTH vs PUNCTURE SIZE



Equivalent Diameter of Puncture, d (mm)

Figure 30: alpha versus delta* for a range of spill sizes

Figure 31: maximum concentration versus delta for a range of river cross-sectional

areas

Lakes or Still Water Bodies

Figure 32: volume versus radius for a hazard zone for a range of lake depths

Figure 33: average concentrations versus volume for the hazard zone for a range of

spill sizes

The flow chart in Figure 25 outlines the steps required to estimate downriver concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 26 through 31) are described in the following subsections.

Nomograms for Non-tidal Rivers.

Figure 26: Time versus distance. Figure 26 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest, at some distance (X) downstream of the spill, can be readily obtained from Figure 26.

Figure 27: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d).

The hydraulic radius (r) for the channel is required in order to estimate the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 27 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 28: Diffusion coefficient versus hydraulic radius. Figure 28 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 27 and the average stream velocity (U).

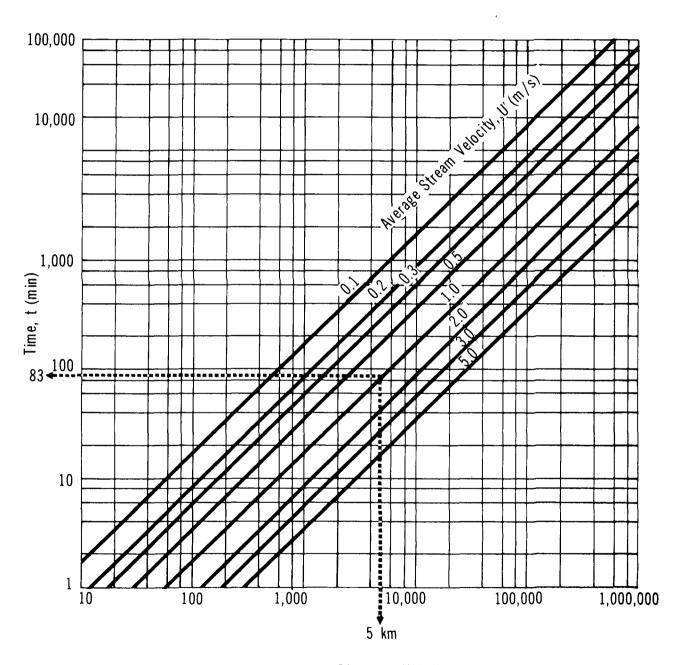
Figure 29: Alpha versus diffusion coefficient. Figure 29 is used to estimate a conversion factor alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 30: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 29 to allow determination of pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and spill size.

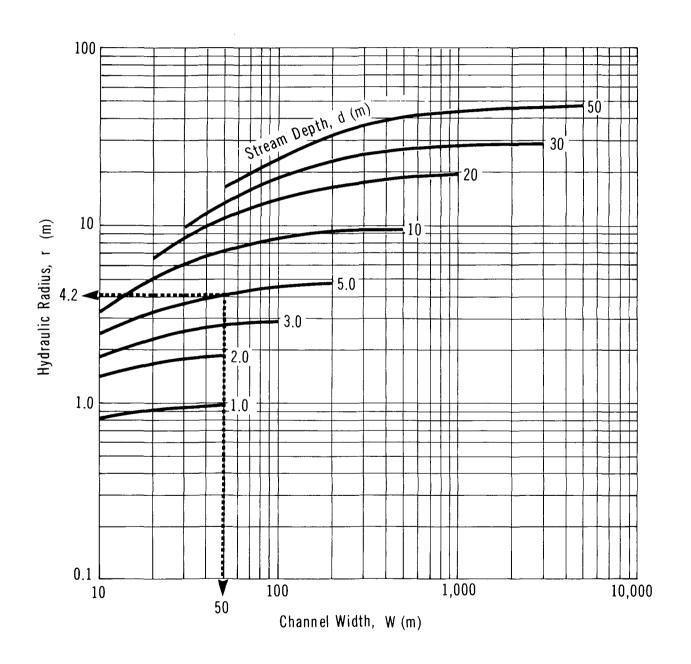
^{*} Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

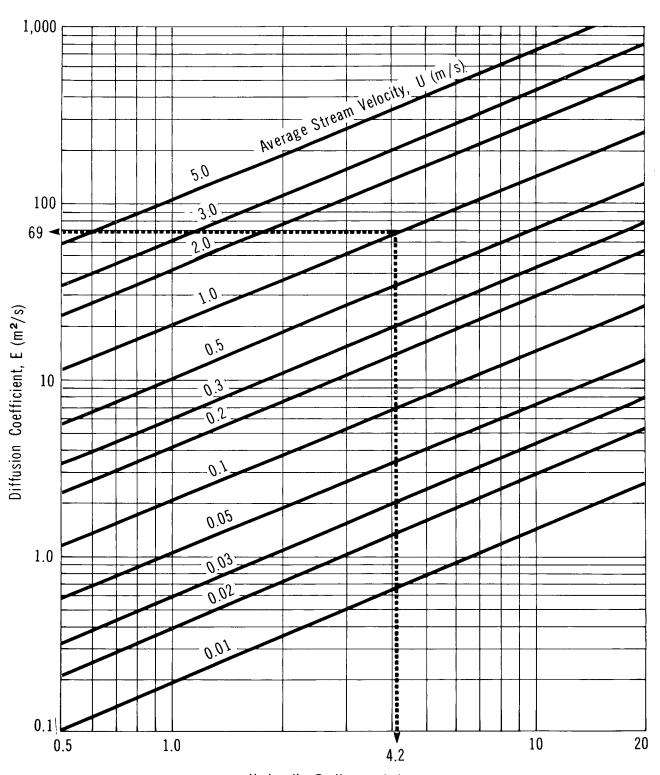
FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS

| SPILL | |
|---|--|
| DEFINE PARAMETERS | Step 1: Observed or Estimated |
| STREAM WIDTH (W) | . W = m |
| STREAM DEPTH (d) | d = m |
| AVERAGE VELOCITY (U) | U = m/s |
| SPILL MASS | MASS = tonnes |
| DOWNSTREAM DISTANCE (X) | X = m |
| CALCULATE TIME (t) TO REACH POINT OF INTEREST | Step 2: Use Figure 26 t = minutes |
| CALCULATE HYDRAULIC | Step 3: Use Figure 27 |
| RADIUS (r) OF CHANNEL | r = m |
| CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E) | Step 4: Use Figure 28 E = m |
| CALCULATE ALPHA (α) AT TIME (t) | Step 5: Use Figure 29 $\alpha = \underline{\hspace{1cm}}$ |
| CALCULATE DELTA (△) FOR SPILL MASS | Step 6: Use Figure 30 Δ = |
| COMPUTE A = W × d | Step 7: Compute stream cross-sectional Area (A) A = W × d m ² |
| CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A) | Step 8: Use Figure 31 C = ppm |

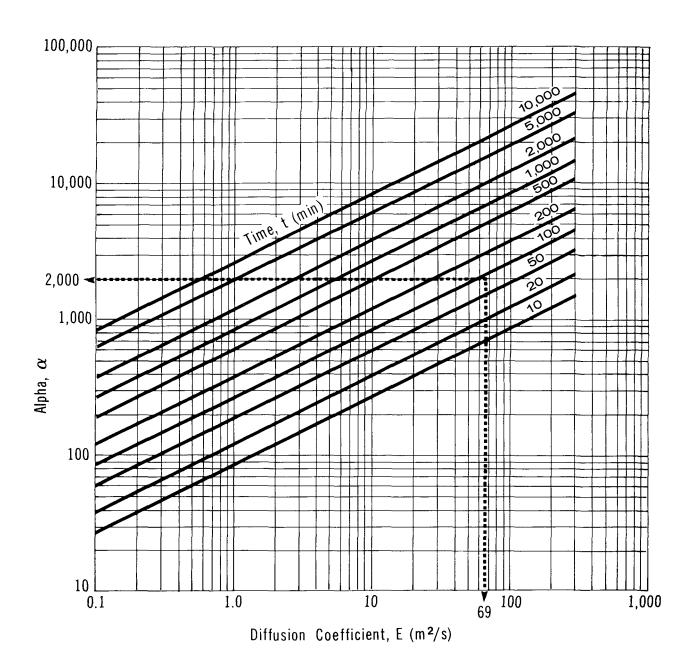


Distance, X (m)





Hydraulic Radius, r (m)



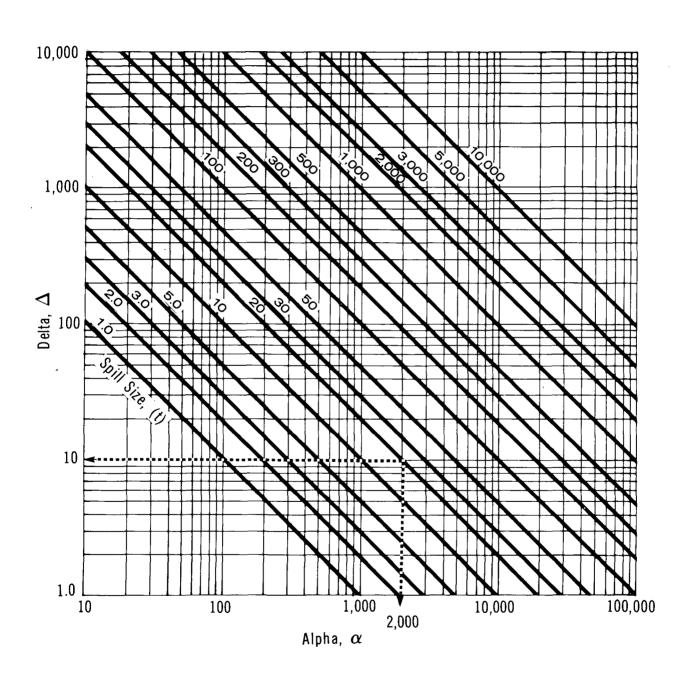


Figure 31: Maximum concentration versus delta. Figure 31 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 31 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

Nomograms for Lakes or Still Water Bodies.

Figure 32: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 32. The radius (r) represents the distance from the spill to the point of interest.

Figure 33: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 33 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

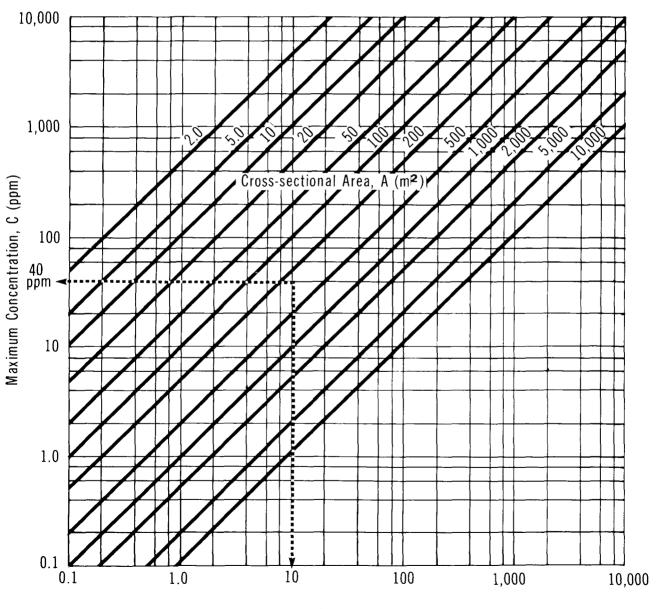
5.4.3 Sample Calculations.

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

Solution

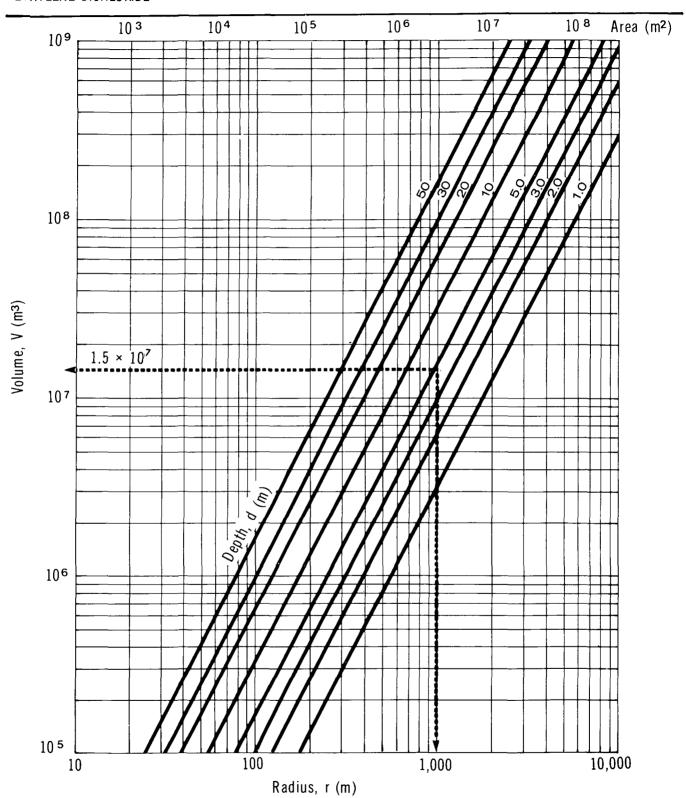
- Step 1: Calculate terminal fall velocity (V_t)
 - . Use Figure 21
 - With d = 200 mm and U < 1 m/s, $V_t = 0.33 \text{ cm/s}$
- Step 2: Calculate settling time
 - Use Figure 22
 - With $V_t = 0.33$ cm/s and d = 10 m, t = 50 min
- Step 3: Calculate distance downstream for smallest droplets
 - . Use Figure 23

MAXIMUM CONCENTRATION vs DELTA



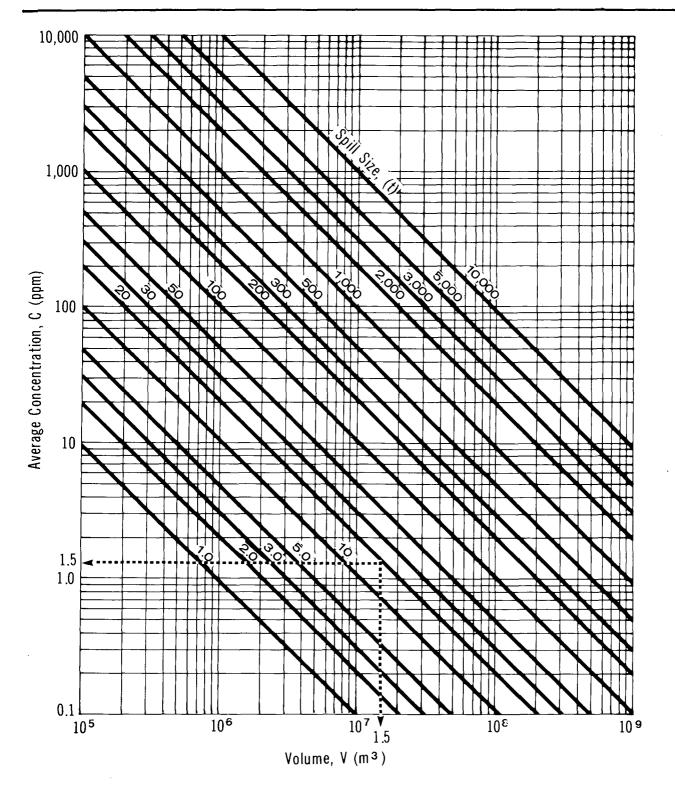
Delta, Δ

VOLUME VS RADIUS



ETHYLENE DICHLORIDE

AVERAGE CONCENTRATION VS VOLUME



- With t = 50 min and U = 0.5 m/s, X = 1,500 m
- Step 4: Calculate maximum spill width
 - . Use Figure 24
 - With d = 200 mm and d = 10 m, W = 58 m
- **5.4.3.2 Pollutant concentration in non-tidal river.** A 20 tonne spill of ethylene dichloride has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

- Step 1: Define parameters
 - W = 50 m
 - $d = 5 \, \text{m}$
 - U = 1 m/s
 - X = 5,000 m
 - Spill mass = 20 tonnes
- Step 2: Calculate time to reach point of interest
 - . Use Figure 26
 - With X = 5,000 m and U = 1 m/s, t = 83 min
- Step 3: Calculate hydraulic radius (r)
 - . Use Figure 27
 - With W = 50 m and d = 5 m, r = 4.2 m
- Step 4: Calculate longitudinal diffusion coefficient (E)
 - . Use Figure 28
 - With r = 4.2 m and U = 1 m/s, E = 69 m²/s
- Step 5: Calculate alpha (α)
 - Use Figure 29
 - With E = 69 m²/s and t = 83 min, α = 2,000
- Step 6: Calculate delta (Δ)
 - Use Figure 30
 - With alpha (α) = 2,000 and spill mass = 20 tonnes, delta (Δ) = 10
- Step 7: Compute stream cross-sectional area (A)
 - $A = W \times d = 50 \times 5 = 250 \text{ m}^2$
- Step 8: Calculate maximum concentration (C) at point of interest
 - Use Figure 31

- With $\Delta = 10$ and A = 250 m², C = 40 ppm
- 5.4.3.3 Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of ethylene dichloride has occurred in a lake. The point of interest is located on the shore approximately 1,000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected under worst case situations?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1,000 m
- spill mass = 20 tonnes

Step 2: Determine the volume of water available for dilution

- Use Figure 32
- With r = 1,000 m, d = 5 m, the volume is approximately 1.5 x 10^7 m³

Step 3: Determine the average concentration

- . Use Figure 33
- . With $V = 1.5 \times 10^7 \text{ m}^3$ and spill mass = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Introduction. The general principles of contaminant transport in soil and their application to this work are described in the Introduction Manual. Specific items related to ethylene dichloride and the development of nomograms for it are presented below.

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

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

comparison to oil spilled onto soil surfaces (Blokker 1971; Freeze and Cherry 1979). Such a model is felt to produce reasonably accurate results despite differences in properties.

It is assumed that when the spill occurs, the soil contains water only up to its field capacity and that this condition prevails down to the groundwater table. The spilled ethylene dichloride fills the pores at the soil surface and begins to penetrate downward. It is assumed that the liquid moves downward through the soil as a saturated slug, leaving behind a constant residual amount (S_0) within the soil pores.

Downward transport will continue until the volume of ethylene dichloride spilled per unit area (B_0) equals the amount retained in the soil as S_0 . Some lateral spreading may occur due to capillary action. If B_0 is greater than the volume that can be retained as S_0 above the groundwater table, the excess liquid will reach the saturated groundwater capillary fringe. Ethylene dichloride is denser than water and thus it will continue to move slowly downward in the water saturated zone. This is shown schematically in Figure 34.

- 5.5.2 Equations Describing Ethylene Dichloride Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.
- 5.5.3 Saturated Hydraulic Conductivity of Ethylene Dichloride in Soil. The saturated hydraulic conductivity (K_0) in m/s is given by:

$$K_0 = \frac{(\rho g)k}{u}$$

where:

k = intrinsic permeability of the soil (m²)

 ρ = mass density of the fluid (kg/m³)

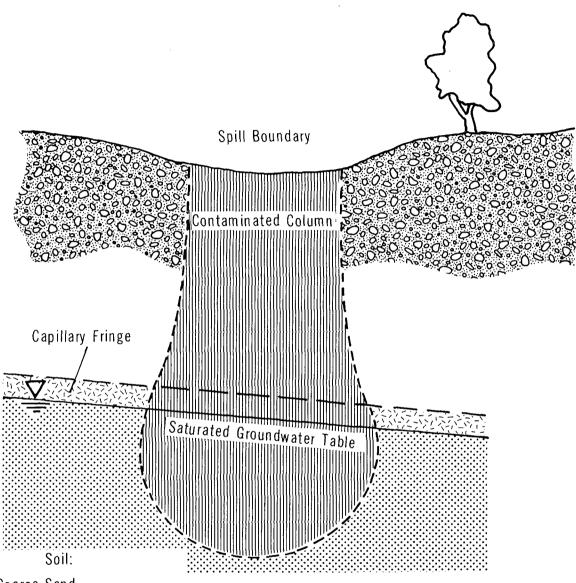
 μ = absolute viscosity of the fluid (Pa•s)

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

The appropriate properties of ethylene dichloride are given in the chart below.

ETHYLENE DICHLORIDE

SCHEMATIC SOIL TRANSPORT



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

| | Ethylene Dichloride | | |
|--|-----------------------------|-----------------------------|--|
| Property | 20°C | 4°C | |
| Mass density (ρ), kg/m ³ | 1,250 | 1,280 | |
| Absolute viscosity (μ), Pa•s | 0.8×10^{-3} | 1.0×10^{-3} | |
| Saturated hydraulic conductivity (K_0) , m/s | (1.53 x 10 ⁷) k | (1.25 x 10 ⁷) k | |

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

| • | Soil Type | | | |
|---|-------------|------------|-----------|--|
| Property | Coarse Sand | Silty Sand | Clay Till | |
| Porosity (n), m ³ /m ³ | 0.35 | 0.45 | 0.55 | |
| Intrinsic permeability (k), m ² | 10-9 | 10-12 | 10-15 | |
| Field capacity (9 _{fC}), m ³ /m ³ | 0.075 | 0.3 | 0.45 | |
| So (residual fraction), m ³ /m ³ | 0.05 | 0.1 | 0.2 | |

Penetration Nomograms. Nomograms for the penetration of ethylene dichloride into the unsaturated zone above the groundwater table were prepared for each soil. The nomograms show the total depth of penetration (B) versus penetration time (t_p) for various volumes spilled per unit area of soil (B_0) . Temperatures of 4°C and 20°C were used. Calculations were based on the equations developed in the Introduction Manual. A flow chart for use of the nomograms is shown in Figure 35. The nomograms are presented in Figures 36, 37 and 38.

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

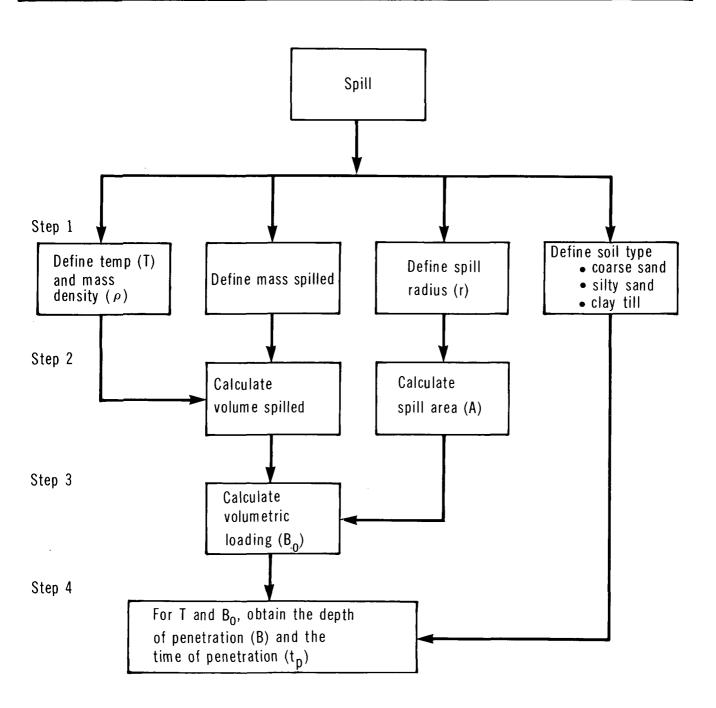
Solution

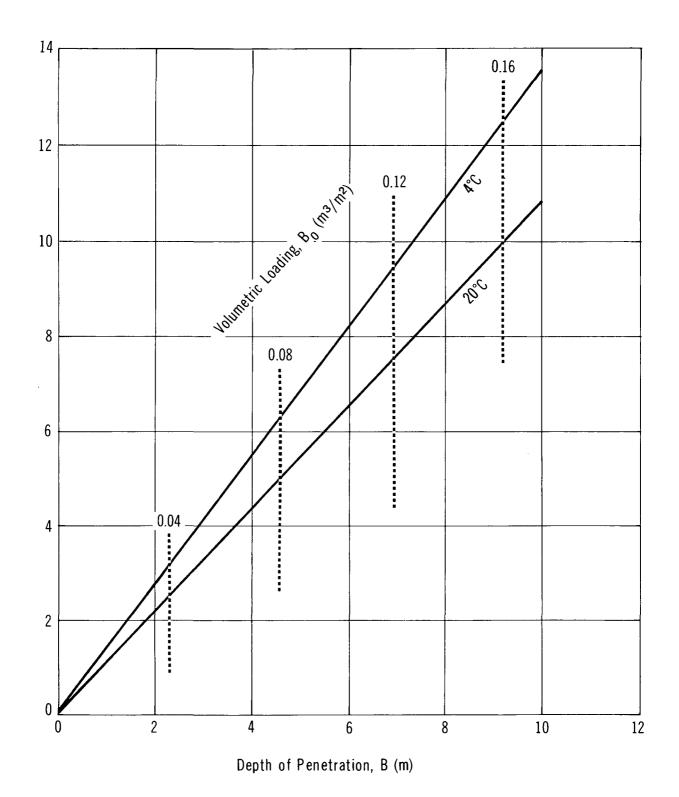
Step 1: Define parameters

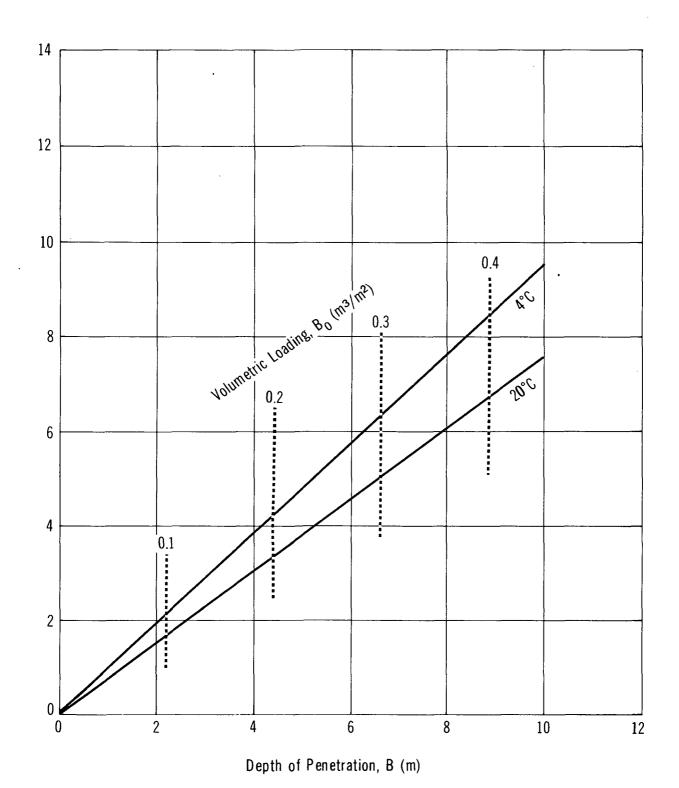
Mass spilled = 20,000 kg (20 tonnes)

ETHYLENE DICHLORIDE

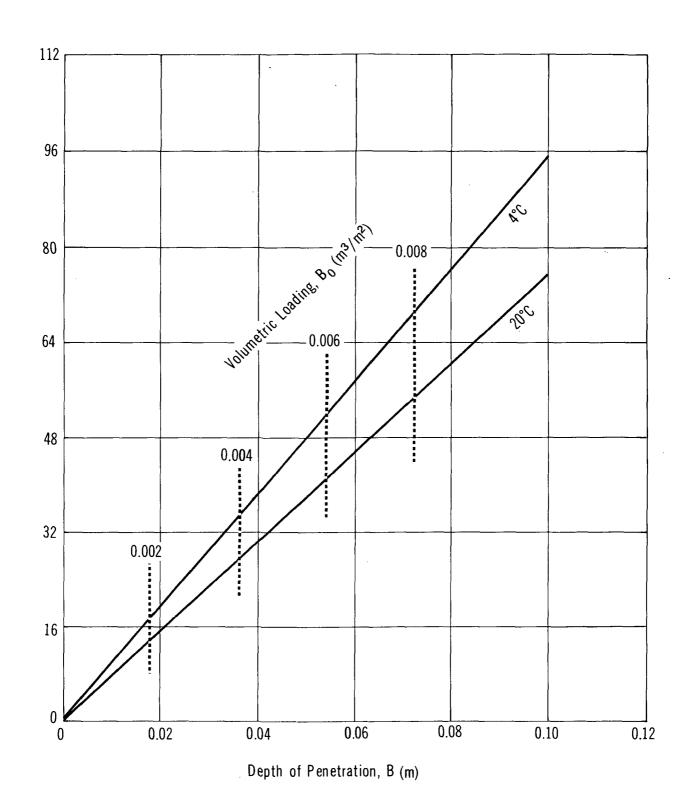
FLOWCHART FOR NOMOGRAM USE







ETHYLENE DICHLORIDE



- $T = 20^{\circ}C$
- . Mass density = $1,250 \text{ kg/m}^3$
- r = 8.6 m
- Step 2: Calculate volume and area of spill

$$V = \frac{M}{E} = \frac{2 \times 10^4 \text{ kg}}{1,250 \text{ kg/m}^3} = 16 \text{ m}^3$$

- $A = \pi r^2 = 232 \text{ m}^2$
- Step 3: Calculate volumetric loading Bo

$$B_0 = \frac{V}{A} = \frac{16}{232} = 0.07 \text{ m}^3/\text{m}^2$$

- Step 4: Estimate depth of penetration (B) and time of penetration (t_D)
 - For coarse sand, $B_0 = 0.07 \text{ m}^3/\text{m}^2$
 - B = 4 m, t_p = 4.2 min

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

- **6.1.1 Water.** None in Canada. In Europe, a provisional limit of 10 mg/L has been recommended (MHSSW 1976). In the United States, the EPA criterion to protect freshwater aquatic life is 3,900 μ g/L (24-h average); concentration should not exceed 8,800 μ g/L at any time. For saltwater aquatic life, the corresponding criteria are 880 μ g/L and 2,000 μ g/L (PTP 1980).
- **6.1.2 Air.** No specific limits have been promulgated or recommended in Canada or the United States.

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. None assigned.

6.2.2 Measured Toxicities.

| Conc. (mg/L) | Time (hours) | Species | Results | Water Conditions | Reference |
|-----------------------------------|------------------------------|--|--|--|-------------|
| Fish Toxic | ity Tests | | | | |
| 175 | 96 | Rainbow trout | LC ₅₀ | unaerated, static repla- cement very soft (t. alk 2.5) 12°C, pH 6.4 | Watts 1982 |
| 155 | 96 | Rainbow trout | LC ₅₀ | unaerated, very soft (t. alk 2.5) 2.1°C, pH 6.4 | Watts 1982 |
| pure chemical | 1 | Eyed coho eggs | 100% lethal | | Morgan 1982 |
| 320-560 150 150 56 56 | 8d 21d 9d 21d 9d | Eyed coho eggs Eyed coho eggs Coho alevins Eyed coho eggs Coho alevins | 100% lethal 46% dead 100% lethal 96% hatch 100% lethal | 3°C, pH 5.5 very soft water static replacement | Morgan 1982 |

| Conc. (mg/L) | Time (hours) | Species | Results | Water Conditions | Reference |
|-----------------|-----------------|----------------------------|------------------|---------------------|---------------|
| Fish Toxic | city Tests | | | | |
| 550 | 96 | Bluegill | TL 50 | static | OHM-TADS 1981 |
| 225 | 96 | Rainbow trout (size-1.8 g) | LC ₅₀ | 13°C | Johnson 1980 |
| 150 to 175 | not stated | Sea perch | LC ₅₀ | | MHSSW 1976 |
| 5 | 24 | Bluegill | no effect | | APOP 1975 |
| 5 | 24 | Rainbow trout | no effect | | APOP 1975 |
| 500 | not stated | Fathead minnow | LC ₅₀ | | APOP 1975 |
| 150 | not stated | Pin Perch | TL_{m} | aerated | WQC 1963 |
| Invertebra | ites | | | | |
| >100 | 96 | G. fasciatus (Scud) | LC ₅₀ | 21°C | Johnson 1980 |
| >100 | 96 | Pteronarcys (Stonefly) | LC ₅₀ | 15°C | Johnson 1980 |
| 320 | 24 | Brime shrimp | TLm | static | Price 1974 |

6.3 Toxicity to Other Biota. Ethylene dichloride is toxic to vertebrates, invertebrates, plants and microorganisms (Drury 1980).

6.3.1 Livestock.

| Conc. (mg/L) | Time (hours) | Species | Route | Result | Reference |
|-----------------|-----------------|---------|------------|--------|----------------|
| 3,000 | 7 | Pig | inhalation | LDLO | Patterson 1976 |

6.3.2 Plants. Ethylene dichloride volatilizes readily into the atmosphere (Fishbein 1980). It is harmful to plants and is known to retard growth and development of the seedling, induce morphological and chlorophyll mutations, and in some cases completely arrest growth, resulting in necrosis and atrophy (Kirichek 1979). Ethylene dichloride has been found to be a weak mutagen in some bacteria and certain grains (Drury 1980).

6.4 Degradation

6.4.1 B.O.D.

| Conc. (kg/kg) | B.O.D. (% Theor.) | Days | Seed | Method | Reference |
|------------------|----------------------|---------|------------------|----------------|-------------|
| | 0 | 20 | | BOD | APOP 1975 |
| | 0 | 5 | sewage seed | freshwater BOD | Price 1974 |
| | 18 | 10 | sewage seed | freshwater BOD | Price 1974 |
| | 7 | 5 to 15 | sewage seed | saltwater BOD | Price 1974 |
| | 15 | 20 | sewage seed | saltwater BOD | Price 1974 |
| | 40 | 10 | non-flocculating | BOD | Ludzak 1960 |
| 0.002 | | 5 | sewage seed | | Ludzak 1960 |
| 1.05 | | 10 | sewage seed | | Ludzak 1960 |

Ethylene dichloride is highly toxic to anaerobic digestion even in very small quantities (150 to 500 mg/L) (Hovius 1973).

- **6.4.2 Chemical Degradation.** The half-life of ethylene dichloride in water is estimated to be on the order of thousands of years on the basis of degradation alone (EPA 560-5-77-003). Volatilization is the most significant route of removal from natural water.
- 6.4.3 Other Studies. It is estimated that the atmospheric half-life of ethylene dichloride is 3 to 4 months. The stability estimate is based on the reaction of ethylene dichloride with free hydroxy radicals (EPA 600-9-75-008). The atmospheric retention time is estimated in another study to be 53 days, with the degradation products being CIHCHO, H₂CCICOC1, H₂CO and H₂CCICHO. The reaction rate (hydroxyl radical reaction rate constant) for the product in the environment is estimated to be 0.22 cm³· molecule-1·sec-1 (EPA 600 3-83-084).

6.5 Long-term Fate and Effects

Ethylene dichloride has a bioaccumulation potential estimated at 9 (APOP 1975). It is slightly lipophilic in biological systems and has a slight tendency to bioaccumulate in fat (EPA 560-5-77-003). It is subject to some biodegradation (OHM-TADS 1981).

7 HUMAN HEALTH

There is a considerable amount of information in the published literature concerning the toxicological effects of exposures of ethylene dichloride on test animals and humans. This chemical has been linked with potentially serious health effects involving the nervous, respiratory, hepatic, renal and cardiovascular systems. Human deaths have been reported in the literature resulting from skin, ingestion and inhalation exposures.

In addition, recent studies have demonstrated that ethylene dichloride is carcinogenic in rats and mice and mutagenic in bacterial tests. Abnormally high numbers of embryonic deaths have been reported in pregnant animals exposed to this chemical.

The USA-NIOSH recommendations for an occupational exposure standard for ethylene dichloride published in 1976 were revised downwards in 1978. Since it causes progressive malignant disease of various organs in two species of animals, NIOSH recommends that ethylene dichloride be considered carcinogenic in man. Ethylene dichloride has been reported in the EPA TSCA Inventory and was listed in the USDHHS Second Annual Report on Carcinogens 1981.

The toxicological data summarized here have been gleaned from reliable standard reference sources and are representative of information in the literature. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. Only acute (short-term) exposure data are given for non-human mammalian species (with the exceptions of Sections 7.4.4 and 7.4.5) to support interpretation of the human data, where appropriate.

7.1 Recommended Exposure Limits

The USA-NIOSH exposure standards for ethylene dichloride are based upon its mutagenic and carcinogenic properties. The OSHA standard has been adopted for toxic effects other than cancer. Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise.

| Guideline (Time) | Origin | Recommended Level | Reference |
|------------------|--------------|--------------------------------|------------|
| Time-weighted Av | erages (TWA) | | |
| TLV * (8 h) | USA-ACGIH | 10 ppm (40 mg/m ³) | TLV 1983 |
| TWA (10 h) | USA-NIOSH | 1 ppm (4 mg/m^3) | NIOSH 1978 |

| Guideline (Time) | Origin | Recommended Level | Reference |
|---|-----------------------|---------------------------------|------------------|
| Time-weighted Ave | rages (TWA) | | |
| PEL (8 h) | USA-OSHA | 50 ppm (200 mg/m ³) | NIOSH Guide 1978 |
| Permissible Concentration (8 h) | B.C. | 50 ppm (200 mg/m ³) | B.C. 1980 |
| Concentration moyenne (mean) | Quebec | 50 ppm (200 mg/m ³) | Quebec 1979 |
| TWAEC (40 h/wk)1 | Ontario (proposed) | 10 ppm (40 mg/m ³) | Ontario 1981 |
| Short-term Exposur | e Limits | | |
| STEL | USA-ACGIH | 15 ppm (60 mg/m ³) | TLV 1983 |
| Ceiling (15 min sample) | USA-NIOSH | 2 ppm (8 mg/m ³) | NIOSH 1978 |
| Ceiling | USA-OSHA | 100 ppm | NIOSH 1978 |
| Maximum Allow- able Peak (not more than 5 min/3 h) | USA-OSHA | 200 ppm | NIOSH 1978 |
| Permissible Concentration (15 min) | B.C. | 75 ppm (300 mg/m ³) | B.C. 1980 |
| Concentration maximale (maximum) | Quebec | 75 ppm | Quebec 1979 |
| STEC (15 min, not more than 4 h/d, 60 min elapsed from time of last exposure to such concentration) | Ontario (proposed) | 15 ppm (61 mg/m ³) | Ontario 1981 |
| Other Human Toxic | ities | | |
| IDLH | USA-NIOSH | 1,000 ppm | NIOSH Guide 1978 |
| TCLLO | | 4,000 ppm (1 h) | RTECS 1979 |
| LDLO | | 845 mg/kg | GE 1979 |
| LDLO | | 810 mg/kg | RTECS 1979 |

¹ TWAEC - Time-weighted Average Exposure Concentration

| Guideline (Time) | Origin | Recommended Level | Reference |
|--------------------|--------|-------------------|-----------------------|
| Other Human Toxici | ties | | |
| LD _{LO} | | 500 mg/kg | TDB (on-line) 1981 |
| TD_{LO} | | 428 mg/kg | RTECS 1979 |

Inhalation Toxicity Index

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

ITI = 1,315.12 (Vapour Pressure, in mm Hg)/(TLV,® in ppm)

At 20° C, ITI = 1,315.12 (66 mm Hg)/(10 ppm)

At 20°C, ITI = 8.7×10^3

7.2 Irritation Data

7.2.1 Skin Contact.

Note:

Human exposure to ethylene dichloride can occur through skin absorption. See Section 7.4.3.

| Exposure Level | | |
|------------------------------------|---|----------------------------------|
| (and Duration) | Effects | Reference |
| SPECIES: Human | | |
| Unspecified concentration (Liquid) | Will burn skin | CHRIS 1978 |
| Unspecified concentration (Liquid) | Severe dermatitis, necrosis of epidermis of feet, accompanied by suppuration and delayed healing. (Worker spilled ethylene dichloride on his socks) | Rosenbaum 1947. IN NIOSH 1976 |

| Exposure Level (and Duration) | Effects | Reference |
|--|--|---|
| SPECIES: Human | | |
| Unspecified concentration (Liquid) | Irritation of mucous membranes, dermatograph-ism, nausea, weakness, and abdominal pain | Brzozowski et al. 1954. <u>IN</u> NIOSH 1976 |
| Unspecified | Repeated contact with liquid can produce a dry scaly, fissured dermatitis | USDHEW 1977 |
| SPECIES: Rabbit | | |
| 2.8 g/kg | LD ₅₀ | Patty 1981 |
| 625 mg (72 h) Non-occluded patch test | Mild irritation | RTECS 1979 |

7.2.2 Eye Contact.

| Exposure Level (and Duration) | Effects | Reference |
|---|--|---|
| SPECIES: Human | | |
| 60 ppm maximum, 15 ppm average (duration not specified) | Conjunctival congestion, burning sensation | Brzozowski et al. 1954. <u>IN</u> NIOSH 1976 |
| Unspecified | Vapour irritating to eyes | CHRIS 1978 |
| Unspecified (Liquid) | May produce corneal injury | CHRIS 1978 |
| Unspecified (Liquid) | Pain, irritation, lacrimation. If promptly removed by washing, no significant injury should occur | Patty 1981 |
| Unspecified | It has been both inferred and erroneously stated that corneal opacities have occurred in humans from ethylene dichloride exposures. Reports of corneal opacities developing in humans exposed to ethylene dichloride have not been found | NIOSH 1976 |

| Exposure Level (and Duration) | Effects | Reference |
|-------------------------------|---|------------|
| SPECIES: Dog | | |
| Unspecified | Clouding of cornea produced by inhalation of vapour | Patty 1981 |
| SPECIES: Fox | | |
| Unspecified | Clouding of cornea produced by inhalation of vapour | Patty 1981 |

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour characteristics: chloroform-like odour

Odour Index: 410 (Verschueren 1977)

| Parameter | Media | Concentration | Reference |
|--------------------------------|----------|--------------------------|------------------|
| Odour Threshold | | 100 ppm | CHRIS 1978 |
| Recognition Threshold | | 40 ppm | GE 1979 |
| Recognition Odour Threshold | In air | 40 ppm | ASTM 1980 |
| Odour Threshold | In water | 29 ppm | ASTM 1980 |
| Odour Threshold | In air | 6 ppm | USDHEW 1967 |
| Odour Threshold | In water | 20 mg/L | Verschueren 1977 |
| Recognition Odour Threshold | In air | 25,000 μg/m ³ | Sullivan 1969 |

7.3.2 Taste. Sweet taste (Merck 1976).

7.4 Long-term Studies

7.4.1 Inhalation.

| Exposure Level (and Duration) | Effects | Reference |
|--|---|---|
| Acute Exposures | | |
| SPECIES: Human | | |
| 3,000 ppm (6 min) | No effect | Verschueren 1977 |
| 1,200 ppm (2 min) | 2 subjects. Noted strong odour but no other subjective or objective responses | Sayers et al. 1930. <u>IN</u> NIOSH 1976 |
| 1,000 ppm (60 min) | No effect | Verschueren 1977 |
| 500 ppm (2,050 mg/m ³) (60 min) | Severe toxic effects | Verschueren 1977 |
| 200 ppm (7 h) | No effect | Verschueren 1977 |
| 100 ppm | Symptoms of illness | Verschueren 1977 |
| 1.5 ppm (30 s) | Temporary stenosis of blood vessels | Borisova 1957, 1960. <u>IN</u> NIOSH 1976 |
| 1.5 ppm (1 min) | Change in depth of breathing | Borisova 1957, 1960. <u>IN</u> NIOSH 1976 |
| Vapour concentration unspecified (few minutes) | Plant engineer entered tank to rescue an employee. Loss of consciousness, death within 6 hours. Some skin absorption likely. Autopsy revealed massive pulmonary edema, hepatic hypertrophy, intense renal congestion | Hadengue and Martin 1953. <u>IN</u> NIOSH 1976 |
| Unspecified (accident- al exposure) | 2 men repairing leaks in pipes carrying ethylene dichloride. Loss of consciousness, with rescue 30 minutes later. Both regained consciousness before death. Autopsy findings included conspicuous jaundice, anemia, slightly swollen kidneys, extensive subepicardial hemorrhages | Brass 1943. <u>IN</u> NIOSH 1976 |

| Exposure Level (and Duration) | Effects | Reference |
|--|---|---|
| SPECIES: Monkey | | |
| 4,500 ppm (10 min) | Loss of balance | Sayers et al. 1930. <u>IN</u> NIOSH 1976 |
| SPECIES: Dog | | |
| 3,000 ppm (2 to 7 h) | Death of 75 to 100% of test animals within 5 days | Heppel et al. 1945. <u>IN</u> NIOSH 1976 |
| SPECIES: Guinea Pig | | |
| 60,000 or 30,000 ppm (30 to 40 min) | Congestion and edema of the lungs, generalized passive congestion of the visceral organs | Sayers et al. 1930. <u>IN</u> NIOSH 1976 |
| 3,000 ppm (2 to 7 h) | Death of 75 to 100% of animals within 5 days | Heppel et al. 1945. <u>IN</u> NIOSH 1976 |
| SPECIES: Rat | | |
| 20,000 ppm (12 min) | No effect | Patty 1981 |
| 12,000 ppm (31.8 min) | LC ₅₀ | Verschueren 1977 |
| 12,000 ppm | Produced various degrees of CNS depression | Patty 1981 |
| 3,000 ppm (2 to 7 h) | Death of 75 to 100% of animals within 5 days. Narcosis | Heppel et al. 1945. <u>IN</u> NIOSH 1976 |
| 3,000 ppm (165 min) | LC ₅₀ | Verschueren 1977 |
| 3,000 ppm (1 h) | No effect | Patty 1981 |
| 3,000 ppm | Definite depression was observed | Patty 1981 |
| Chronic Exposures | in the form of inactivity | |
| SPECIES: Human | | |
| 2,500 ppm (estimated) | Workers frequently cleaned equipment with solution containing 95% ethylene dichloride. Irritation of the conjunctiva and mucous membranes of the respiratory tract and an excita- | Rejsek 1974. <u>IN</u> NIOSH 1976 |

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| | tion resembling the early stages of alcohol intoxication | |
| 200 to 62 ppm | Employees in centrifuge room at oil refinery. Burning sensa- tion of the eyes and lacrimation. Dryness of the mouth, dizziness, an unpleasant sweet aftertaste, constipation, loss of appetite, and epigastric pain | Cetnarowicz 1959. <u>IN</u> NIOSH 1976 |
| 200 to 62 ppm | Employees in centrifuge room at oil refinery. Elevated urobilinogen levels, abnormal percentile distribution of white blood cells, high serum bilirubin levels, elevated nonprotein nitrogen levels, diminished amounts of albumin in the serum, elevated globulin levels, positive Takata-Ara tests, and delayed return to normal values in the glucose tolerance test | Cetnarowicz 1959. <u>IN</u> NIOSH 1976 |
| 125 to 75 ppm (2 to 3 wk) | Fatalities after 2 or more acute poisonings in a 2- to 3-week period. Early symptoms include general weakness, headache, dizziness, vomiting (usually with a trace of bile) and irritation of the mucous membranes and skin | Rosenbaum 1974. <u>IN</u> NIOSH 1976 |
| 120 ppm (estimated) (70 to 85 min/d for 9 mo) | After 3 weeks, anorexia, epi- gastric pains, fatigue, irrit- ability, and nervousness. As the exposure progressed, development of headaches, sexual impotence, insomnia, feelings of drunkenness, tingling sensations of the eyes, weight loss, exaggerated dampness of the skin, devia- tion to the right in a blind walk and a slight trembling of the hands | Guerdjikoff 1955. <u>IN</u> NIOSH 1976 |

| Exposure Level (and Duration) | Effects | Reference |
|--|--|---|
| 100 to 70 ppm (7.5 h/d, chronic) | Delayed effects occurred after the evening meal. These varied from lassitude and malaise to nausea, vomiting and abdominal pain | Byers 1943. <u>IN</u> NIOSH 1976 |
| 25 ppm (chronic) | No chronic effects on the blood picture or on individual organs were established. Frequent findings were bradycardia (heart rate 60 beats/min or less) and bright red, long-lasting dermographism, considered to be transitory CNS effects. There were nervous system functional disturbances of varying intensity, heightened liability of the autonomic nervous system, muscular torus, increased hidrosis, and frequent complaints about fatigability, irritability and sleeplessness | Rosenbaum 1939. <u>IN</u> NIOSH 1976 |
| 15 ppm average, 60 ppm peak (skin absorption of the liquid was also significant) | Weakness, reddenning of the pharynx, bronchial symptoms, metallic taste, headache, nausea, cough, liver pain, hastened pulse, and dyspnea after effort. Agri- cultural workers were exposed to atmospheric concentrations in the field and were also exposed to direct contact when liquid spilled on their clothing and skin. Used ethylene dichloride to wash their skin | Brzozowski et al. 1954. <u>IN</u> NIOSH 1976 |
| 15.5 ppm (female) | Ethylene dichloride found in the milk of nursing women. Concentration ranged from 0.54 to 0.64 mg/L | Urusova 1953. <u>IN</u> NIOSH 1976 |

Exposure Level

| (and Duration) | Effects | Reference |
|---|--|--|
| 15 to 10 ppm average, greater than 40 ppm peak, chronic | Impairment of the central nervous system and increased morbidity, especially diseases of the liver and bile ducts | Kozik 1957. <u>IN</u> NIOSH 1976 |
| 7.4.2 Ingestion. | | |
| Exposure Level (and Duration) | Effects | Reference |
| Acute Exposures | | |
| SPECIES: Human | | |
| 200 to 150 mL | Deaths occurred at 10, 15, 33 and 35 hours after ingestion. Autopsy findings: punctuate hemorrhaging in the epicardium, pleura and mucous membranes of the stomach and duodenum. Varying degrees of liver damage, yellow-white fibrinous bundles of blood in the heart cavities and lesser circulatory vessels, distinct icteric colouring of the endocardium, aortal intima and dura mater, and evidence of decomposition of circulating erythrocytes | Bryzhin 1945. <u>IN</u> NIOSH 1976 |
| 50 g | Lengthening of the prothrombin time (Quick's test), decrease in clotting factors II and V and in thrombocytes. Death from circulatory shock after 17 hours (1 subject) | Schonborn 1970. <u>IN</u> NIOSH 1976 |
| Liquid "small amount" | Group of soldiers who drank liquid developed headaches, nausea, but were not sick enough to seek medical help | Ienistea and Mezincesco 1943. <u>IN</u> NIOSH 1976 |

| Exposure Level (and Duration) | Effects | Reference |
|-------------------------------|---|-------------------------------------|
| Liquid "small amount" | Victim experienced vomiting, diarrhea. Hospitalized 2nd day after ingestion. Cyanotic, weak heart beat. Kidney and liver damage. Recovered by 2 weeks after ingestion | Bloch 1946. <u>IN</u> NIOSH 1976 |
| SPECIES: Rabbit | and after ingestion | |
| 860 mg/kg | LD ₅₀ | RTECS 1979 |
| SPECIES: Rat | | |
| 5 to 0.5 g/kg | LD ₅₀ | CHRIS 1978 |
| 770 mg/kg | LD ₅₀ | Doc. TLV 1981 |
| 0.68 g/kg | LD ₅₀ | Verschueren 1977 |
| SPECIES: Mouse | | |
| 600 mg/kg | LDLO | RTECS 1979 |

7.4.3 Skin Contact. Significant absorption of ethylene dichloride may result from skin contact.

| Exposure Level (and Duration) | Effects | Reference |
|---|--|---|
| SPECIES: Human | | |
| Concentration not speci- fied, chronic exposure to liquid | Agricultural workers were exposed to liquid spilled on their skin and clothing. They also washed their skin with ethylene dichloride. Symptoms following exposure included nausea, weakness, abdominal pain and irritation of mucous membranes | Brzozowski et al. 1954. <u>IN</u> NIOSH 1976 |

| Exposure Level (and Duration) | Effects | Reference |
|------------------------------------|---|---|
| Unspecified concentration (Liquid) | Employees' overalls saturated when splashed with liquid. Liquid also entered one eye. Victim was dazed, experienced retching, vomiting for 9 hours. Violent epigastric pain | London. His Majesty's Stationery Office 1946. IN NIOSH 1976 |

7.4.4 Carcinogenicity.

| | • | |
|--|---|--|
| Exposure Level (and Duration) | Effects | Reference |
| SPECIES: Rat | | |
| 150 ppm | No relevant changes in the incidence of tumors apart from a moderate overall increase in benign mammary tumors | Maltoni 1978. <u>IN</u> NIOSH 1978 |
| 300 & 150 mg/kg (female) 200 & 100 mg/kg (female) (5 d/wk for 78 wk) | A few gross tumors were found | Weisburger, written communication 1976. IN NIOSH 1976 |
| 100 or 50 mg/kg (5 d/wk for 78 wk) | A few animals with tissue masses | Weisburger, written communication 1976. IN NIOSH 1976 |
| 100 mg/kg (by intragastric intubation) | Male rats: 7/50 with hemangio- sarcomas, 6/50 fibroma of subcutaneous tissue and 9/50 squamous cell carcinoma. Female rats: 18/50 had mamma- ry carcinoma, 4/50 hemangio- sarcoma and 24/50 mammary carcinoma or adenoma | NIOSH 1978 |
| 50 mg/kg (by intragastric intubation) | Male rats: 9/50 with hemangio- sarcomas, 5/50 fibroma of sub- cutaneous tissue and 3/50 squa- mous cell carcinoma. Female rats: 1/50 with mammary carci- noma, 4/50 hemangiosarcoma and and 15/50 mammary carcinoma or adenoma | NIOSH 1978 |

| Exposure Level (and Duration) | Effects | Reference |
|---|--|------------|
| SPECIES: Mouse | | |
| 100 mg/kg (by intra- gastric intubation) | Male mice: 15/48 with lung adenomas and 12/48 hepatocellular carcinomas. Female mice: 15/48 lung adenomas, 7/48 mammary carcinoma and 5/47 stromal polyp or sarcoma | NIOSH 1978 |
| 50 mg/kg (by intra- gastric intubation) | Male mice: 1/47 with lung adenomas, and 6/47 hepatocellular carcinomas. Female mice: 7/50 with lung adenomas, 9/50 mammary carcinoma and 5/49 stromal polyp or sarcoma | NIOSH 1978 |

7.4.5 Mutagenicity and Teratogenicity.

| Exposure Level | | | | |
|---|---|--|--|--|
| (and Duration) | Effects | Reference | | |
| SPECIES: Rat | | | | |
| 300, 100 or 0 ppm (d 6 through 15 of gestation) | Severe maternal toxicity at 300 ppm, 2/3 of dams died. No signs of toxicity at 100 ppm. No adverse effects on embryonal or fetal development at 100 ppm | Patty 1981 | | |
| 15 mg/m ³ | Preimplantation embryonic deaths 5 times higher than in controls | Vozovanya 1976. <u>IN</u> NIOSH 1978 | | |
| SPECIES: Drosophila melanogaster | | | | |
| 1,000 ppm | Sex chromosome loss and nondisjunction | RTECS 1979 | | |
| SPECIES: Unspecified | | | | |
| Unspecified | "Moderate mutagen" alone and a "potent mutagen" when applied together with liver enzymes | Rannug and Ramel 1977. <u>IN</u> NIOSH 1978 | | |

7.5 Symptoms of Exposure

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

7.5.1 Inhalation.

- 1. Irritation of mucous membranes.
- 2. Lacrimation.
- 3. Headache.
- 4. Lassitude.
- 5. Insomnia.
- 6. Irritability.
- 7. Dizziness.
- 8. Constipation.
- 9. Hidrosis.
- 10. Nausea.
- 11. Vomiting.
- 12. Drunkenness (CHRIS 1978).
- 13. Anorexia.
- 14. Depression (CHRIS 1978).
- 15. Systemic toxicity affecting liver, digestive tract, kidneys, adrenal glands and nervous system (GE 1979).
- 16. Shock.
- 17. Narcosis.
- 18. Coma.
- 19. Respiratory failure (NIOSH 1976).
- 20. Circulatory failure (NIOSH 1976).
- 21. Death.

7.5.2 Ingestion.

- 1. Irritation of lips, mouth and gastrointestinal tract.
- 2. Dizziness.
- 3. Nausea and vomiting.
- 4. Diarrhea with bloody stool (MCA 1971).
- 5. Mental confusion (USDHEW 1977).

- 6. Pulmonary edema (NIOSH 1976).
- 7. Hyperemia and hemorrhagic lesions of most organs including stomach, intestines, heart, brain, liver and kidney.
- 8. Shock.
- 9. Narcosis.
- 10. Death.

7.5.3 Skin Contact.

- 1. Dry skin. Defatting of the skin (GE 1979).
- 2. Inflammation.
- 3. Moderate edema (MCA 1971).
- 4. Blistering.
- 5. Necrosis (MCA 1971).
- 6. Repeated contact with liquid can produce a dry, scaly, fissured dermatitis (USDHEW 1977).

7.5.4 Eye Contact.

- 1. Irritation.
- 2. Lacrimation.
- 3. Inflammation of conjunctiva.
- 4. Clouding of cornea (GE 1979).
- 5. "It has been erroneously stated that corneal opacities have occurred in humans from ethylene dichloride exposures...." (NIOSH 1976).

7.6 Human Toxicity to Decay or Combustion Products

Degradation products of ethylene dichloride may include carbon monoxide, carbon dioxide, phosgene, and hydrogen chloride (Ullmann 1975).

7.6.1 Carbon Monoxide, Carbon Dioxide, Phosgene, and Hydrogen Chloride. Carbon monoxide is a colourless, practically odourless gas which is a chemical asphyxiant. It causes hypoxia by complexing with hemoglobin and reducing the oxygen-carrying capacity of the blood. Excessive exposures will result in death from asphyxia. More moderate exposures may cause headaches and affect mental functions. The effects of moderate exposures are reversible, although considerable time is required to reverse the carbon-monoxide/hemoglobin complexing reaction. The TLV® for carbon monoxide is 50 ppm (8 h - TWA) and 400 ppm (STEL) (TLV 1983).

Carbon dioxide is a colourless, odourless gas which in elevated concentrations may act to produce mild narcotic effects, respiratory stimulation, and asphyxiation. Its TLV* is 5,000 ppm (8 h - TWA) and 15,000 ppm (STEL) (TLV 1983).

Phosgene is a colourless, nonflammable gas with an odour resembling that of newly mown hay. It is generally accepted that phosgene may cause chronic lung disease in man. It has an irritating effect on the respiratory tract at levels slightly above 0.1 ppm. Tolerance develops with chronic exposures. The TLV® for phosgene is 0.1 ppm (8 h -TWA) (TLV 1983).

Hydrogen chloride may be present as a gas or a liquid. In contact with human skin, it causes irritation, inflammation, burns, blistering dermatitis and profound tissue damage depending upon concentration and length of contact. In contact with eyes, it can cause stinging, burning, opaqueness of the cornea and corneal necrosis. Inhalation causes coughing, choking, ulceration of the mucosa, bronchitis, pneumonia and, in cases of exposure to extremely high concentrations, pulmonary edema and death. The TLV® is 5 ppm (ceiling) (TLV 1983).

8 CHEMICAL COMPATIBILITY

| 8.1 Compat Groups | ibility of Ethyle | ene Dichlori | / [2] | Othe | r Chemicals or Che | mical |
|--|-------------------|--|--|---|---|---|
| | | | 8 \s\z\ | | | |
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| Service of the servic | | }\5\9\9\5\ \\ig\5\\$\\$\\$\ \$\\\\\\\\\\\\\\\\\\\\\\\\\\\\ | \\\ \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\ | \ \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\ | | A LEW |
| GENERAL | | | | | | |
| Heat | x | × | | | | Sax 1979 |
| Fire | x x | × | | | Moderate explo- sion hazard when vapour is expos- ed to a flame | Sax 1979 |
| SPECIFIC CHEMICALS | | | | | | |
| Aluminum | x | | | | Reaction with powdered aluminum or in some cases in a sealed tank caused explosions | Bretherick 1979 |
| Ammonia | x | | | | Can cause an ex- plosion with li- quid ammonia | NFPA 1978 |
| Dimethyl- aminopro- pylamine | | | | x | When mixed with wet ethylene dichloride | NFPA 1978 |
| Dinitrogen Tetroxide (Nitrogen Dioxide) | | | | | | Bretherick 1979 |
| | | | 1 | | | |

8.1 Compatibility of Ethylene Dichloride with Other Chemicals or Chemical Groups (Continued)

| Sold of the sold o | * & S | | 3 3 3 | /0) ₹/3 | | | 0 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 | | // & |
|--|-------|-----------------------------|--------------------|------------|---|--|---|---|--|
| | | 0 \delta \delta 0 | |) | | | i/8) 8/3/ | | put to the state of the state o |
| Nitric Acid | | x | | | | | | Mixtures are easily detonated by heat, impact or friction | Bretherick 1979 |
| Potassium | | x | | | | | | Forms explosive mixtures with halocarbons generally | Bretherick 1979 |
| CHEMICAL GROUPS | | | | | | | | | |
| Alkali and Alkaline Earth Metals | | x | | | | | | | Bretherick 1979; EPA 600/2- 80-076 |
| Mercaptans | x | | | | | | | Form thioethers | EPA 600/2- 80-076 |
| Metal Powders | | x | | | | | x | | EPA 600/2- 80-076 |
| Nitrides | x | | | x | | | | Generates ammonia | EPA 600/2- 80-076 |
| Organic Peroxides | | x | x | | | | | | EPA 600/2- 80-076 |
| Oxidizing Agents | x | | | x | : | | | Yields hydrogen chloride fumes | EPA 600/2- 80-076 |
| Reducing Agents | | x | | | | | | | EPA 600/2- 80-076 |

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

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

- 9.1.1 Fire Concerns. Ethylene dichloride is a flammable liquid. Its vapours form explosive mixtures with air and may travel along surfaces to distant ignition sources and flash back (NFPA 1978; GE 1978). Explosion hazards can exist at elevated temperatures. It may react vigorously with oxidizing materials. Thermal degradation products include highly toxic fumes of phosgene, carbon monoxide, carbon dioxide and hydrogen chloride. Explosions have occurred with mixtures of ethylene dichloride with liquid ammonia or with dimethylaminopropylamine. Finely divided aluminum or magnesium metal may be hazardous in contact with ethylene dichloride (GE 1978).
- **9.1.2** Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to prevent rupture.

Small fires: Dry chemical, CO₂, foam (alcohol) or water spray.

Large fires: Water spray, fog or foam.

Move containers from fire area if this can be done without risk. Stay away from ends of tanks (ERG 1980).

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (GE 1978). Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area and the contents transferred to other suitable containers (MCA 1971). Water spray may be used to diminish vapours and to protect men attempting to stop a leak (NFPA 1978). Fluorocarbon water foam can also be used to diminish vapours and provide wet-down (EPA 670/2-75-042).

Hycar, an absorbent material, has shown possible applicability for vapour suppression and/or containment of ethylene dichloride (ICI 1982).

9.1.3.2 Spills on land. For small spills, soak up with sand, earth, vermiculite or other noncombustible absorbent material and shovel into covered metal containers for disposal (GE 1978).

For larger spills, contain if possible by forming mechanical or chemical barriers to prevent spreading. Fly ash or cement powder can be applied to absorb the liquid bulk. Application of a universal gelling agent to immobilize the spill is also recommended (EPA 670/2-75-042).

Depending on the size of the spill, pick up spilled material with pump or vacuum equipment for recovery or disposal. Carbon or sorbents can be used on remaining portions (OHM-TADS 1981).

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

9.1.4 Cleanup and Treatment.

- 9.1.4.1 Spills on land. If the area of the spill is porous, remove as much contaminated earth as possible and place in closed containers for disposal (PPG MSDS 1980).
- 9.1.4.2 Spills in water. After containment of the spilled material, a universal gelling agent may be applied to solidify the trapped mass and to increase the effectiveness of the berm. If solubilized, activated carbon can be applied at 10 percent of the spill amount over region occupied by 10 mg/L or greater concentrations. The immobilized masses of pollutants can be removed by the use of mechanical dredges or lifts (EPA 670/2-75-042).
- **9.1.4.3** General. The following treatment processes have shown possible applicability for spill countermeasures:

| Process | % Removal (TSA 1980) | Process | Maximum % Removal (EPA 600/8-80-042E) |
|------------------------------|-------------------------|--|---|
| Stripping Solvent extraction | 99 94-100 | Clarification/sedimentation with chemical addition (Alum, Polymer) | >60 |
| Carbon adsorption | 81 | | |

| Process | % Removal (TSA 1980) | Process | Maximum % Removal (EPA 600/8-80-042E) |
|---------|-------------------------|--|---|
| | | Steam stripping | >99 |
| | | Solvent extraction | >99 |
| | | Granular activated carbon adsorption | >99 |
| | | Powdered carbon addition (with activated sludge) | 81 |

- 9.1.5 Disposal. Waste ethylene dichloride must never be discharged into sewers or surface waters. Contaminated soil or sorbents (sand, vermiculite, etc.) should be disposed of at a waste management facility. Recovered liquids may be reprocessed or incinerated or must be treated in a waste management facility (PPG MSDS 1980).
- 9.1.6 Charcoal Filtration Data (EPA 600/8-80-023). The following recommended values for the removal of ethylene dichloride in water by either the single stage powdered carbon contactor or the granular carbon column adsorption system were obtained using the Freundlich adsorption equation. The derivation of the equation is discussed in the Introduction Manual.

| SINGLE STAGE POWDERED CARBON CONTACTOR SYSTEM | | | | |
|---|---------------------|----------------------------|--|--|
| Initial Concentration (mg/L) | Carbon Doses (mg/L) | Final Concentration (mg/L) | | |
| 1.0 | 1,700 | 0.1 | | |
| 1.0 | 13,000 | 0.01 | | |
| 1.0 | 86,000 | 0.001 | | |
| 0.1 | 1,200 | 0.01 | | |
| 0.1 | 8,600 | 0.001 | | |
| 0.01 | 780 | 0.001 | | |

| GRANULAR CARBON COLUMN SYSTEM: (ESTIMATED) | | | | |
|--|--|--|--|--|
| Initial Concentration (mg/L) | Carbon Doses or Requirements (Breakthrough Doses) (mg/L) | | | |
| 1.0 | 280 | | | |
| 0.1 | 190 | | | |
| 0.01 | 120 | | | |

These carbon doses were reported in water with neutral pH.

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

If the spilled material is known to be ethylene dichloride:

- Splash-proof chemical safety goggles, impervious clothing and self-contained breathing apparatus should be worn (PPG MSDS 1980).
- Polyethylene, neoprene or polyvinyl alcohol is recommended for gloves (PPG MSDS 1980).
- Eye wash stations and safety showers should be readily available in areas of use or spill situations (GE 1978).
- The following is a list of respiratory protection recommended for personnel working in areas where ethylene dichloride is present (MCA 1971):
 - . Self-contained breathing apparatus.
 - . Positive pressure hose masks.
 - . Air-line masks, supplied with clean compressed air, suitable for use only where conditions will permit safe escape in case of failure of compressed air supply.
 - . Industrial canister-type gas masks, equipped with full facepieces and approved by the U.S. Bureau of Mines, fitted with the proper canister for absorbing vapour, will afford protection against concentrations not exceeding 2 percent by volume when used in accordance with manufacturer's instructions.
- 9.1.8 Special Precautions. Store in a clean, cool, well-ventilated area. Keep away from heat, sparks or flames. Outside or detached storage of this flammable material is preferred. Store small quantities in brown bottles or opaque containers as this solvent is light-sensitive. Eliminate ignition sources in areas of use or storage. Use spark-proof

tools. Ground and bond metal containers for liquid transfers to prevent static sparks (GE 1978).

9.2 Specialized Countermeasures Equipment, Materials or Systems

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

Chemical/Physical Modification: Ultrox (UV-Ozone) Process

Treating Agent: Hazorb (Sorbent)

10 PREVIOUS SPILL EXPERIENCE

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

10.1 Barge Spill (Personal Communication with Vulcan 1982; HMIR 1981).

Overfilling a river barge caused approximately 1.3 million litres of ethylene dichloride to be spilled into a lake. It was about a month later during a routine inventory that the material was found to be missing. Response personnel used a conductivity meter and analyses of water samples to discover the large pool of concentrated ethylene dichloride, lying in about 10 m of water at the bottom of the lake. The boundaries of the ethylene dichloride pool and its depth at various locations were pinpointed by using a sonar laser device developed by Rockwell International. The pool measured approximately 110 m by 36 m and was up to 0.7 m deep. Water samples taken near the pool revealed concentrations of ethylene dichloride in the parts per billion range.

Cleanup crews arrived on site and developed (on-site) a special suction head fitted with a conductivity meter to determine when the head was immersed in the chemical. A screen was also placed on the suction head to prevent any mud from being pumped. Approximately 1.1 million litres of ethylene dichloride were recovered by this method during a period of about 2 weeks. The recovered material was shipped to a plant for purification and resale.

One environmental effect that resulted from the spilled material was that the ethylene dichloride concentration found in fish at the time of cleanup was in the range of 2 to 4 ppb; a few months after cleanup, the fish contained no detectable ethylene dichloride. Additional water quality monitoring is being undertaken occasionally.

11 ANALYTICAL METHODS

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

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

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

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

11.1 Quantitative Method for the Detection of Ethylene Dichloride in Air

11.1.1 Gas Chromatography (NIOSH 1977). A range of 195 to 819 mg/m³ (48.20 to 202.35 ppm) of ethylene dichloride in air may be determined by adsorption on charcoal, desorption with carbon disulphide, followed by gas chromatographic analysis.

A known volume of air is drawn through a 7 cm long charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The first section contains 100 mg whereas the second section contains 50 mg. A silylated glass wool plug is placed before the front adsorbing section. A sample size of 3 to 10 L is recommended at a flow rate of 200 cm³/min.

The charcoal tube sample is scored before the first section of charcoal and broken. Transfer the larger section of charcoal to a 2 mL stoppered sample container containing 1.0 mL of carbon disulphide. Perform the same operation with the backup section. The samples should be allowed to desorb for 30 minutes. A 5 μ L aliquot is injected into a gas chromatograph equipped with a flame ionization detector. Typical gas chromatograph conditions are: a 10 ft. x 1/8 in. stainless steel column packed with 10 percent OV-101 stationary phase on 100/120 mesh Supelcoport, nitrogen carrier gas

flow at 30 mL/min, hydrogen gas flow at 35 mL/min, air flow at 400 mL/min, injector temperature at 225°C, detector temperature at 250°C, and a column temperature of 70°C. The ethylene dichloride is determined by using an electronic integrator to find the area under the curve in conjunction with a standard curve.

11.2 Qualitative Method for the Detection of Ethylene Dichloride in Air

The sample is collected as in Section 11.1.1 and desorbed. One drop of sample is added to 0.5 mL of ethanol and 5 drops of 20 percent sodium hydroxide is then added. The mixture is then heated for several minutes and then cooled. Dilute nitric acid is added until the solution is acidic. The mixture is then boiled and allowed to cool. Silver nitrate is added drop-wise; a white precipitate indicates the presence of an alkyl halide (Owen 1969).

11.3 Quantitative Method for the Detection of Ethylene Dichloride in Water

11.3.1 Partition Infrared (AWWA 1981). A range of 40 to 400 ppm ethylene dichloride in water may be determined by partition infrared spectroscopy.

A minimum of 1 L of representative sample is collected in an appropriate container. The sample is acidified to pH 2 or lower with dilute hydrochloric acid. A 5 mL volume should be sufficient. The sample is transferred to a separatory funnel and a 30 mL volume of Freon® 113 (1,1,2-dichloro-1,2,2-difluoroethane) is added after it is used to rinse the sample container. The solvent layer is drained into a 100 mL volumetric flask. Two more 30 mL Freon® 113 extracts are carried out and the extracts combined in the 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon® 113.

The sample is scanned on a suitable infrared spectrophotometer from 3,200 cm⁻¹ to 2,700 cm⁻¹ using matched 1 cm near-infrared silica cells. The sample concentration is determined from a calibration curve.

11.4 Qualitative Method for the Detection of Ethylene Dichloride in Water

The sample is collected as in Section 11.3.1. One drop of sample is added to 0.5 mL of ethanol and 5 drops of 20 percent sodium hydroxide is then added. The mixture is heated for several minutes and then cooled. Dilute nitric acid is added until the solution is acidic. The mixture is then boiled and allowed to cool. Silver nitrate is added drop-wise; a white precipitate indicates the presence of an alkyl chloride (Owen 1969).

11.5 Quantitative Method for the Detection of Ethylene Dichloride in Soil

11.5.1 Partition Infrared (AWWA 1981). This method is used for the detection of concentrations greater than 40 ppm ethylene dichloride in soil.

Approximately 20 g of soil, accurately weighed, is placed in a glass jar and dried by the addition of magnesium sulphate. Freon® 113 is used to extract the ethylene dichloride. Three extractions using 30 mL of Freon® 113 each time are carried out. The extracts are combined in a 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon® 113. The sample is scanned on a suitable infrared spectrophotometer from 3,200 cm⁻¹ to 2,700 cm⁻¹. Matched 1 cm near-infrared silica cells are used. The sample concentration is determined from a calibration curve.

11.6 Qualitative Method for the Detection of Ethylene Dichloride in Soil

A suitable soil sample is placed in an extraction flask and extracted with Freon® 113 as in Section 11.5.1. The residue is taken up in ethanol. One drop of dissolved residue is treated with 5 drops of 20 percent sodium hydroxide. The solution is heated for several minutes and then cooled. The solution is acidified with dilute nitric acid and then boiled and allowed to cool. Silver nitrate solution is added and a white precipitate indicates an alkyl chloride (AWWA 1981; Owen 1969).

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EnviroTIPS Common Abbreviations

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