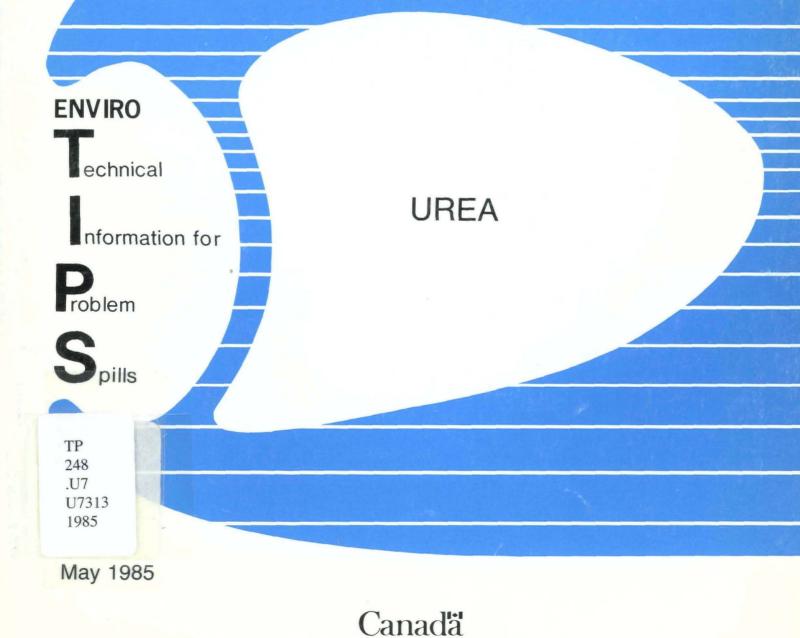


Environment Canada Environmental Protection Service

Environnement Canada Service de la protection de l'environnement



ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

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

EnviroTIPS manuals are available from:

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

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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

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FOREWORD

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

ACKNOWLEDGEMENTS

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

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

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1 SUMMARY

UREA (NH2CONH2)

White granules or prills, or clear liquid.

SYNONY**MS**

Carbamide, Carbonyldiamine, Carbonyl Diamide, Carbamimidic Acid

TRADE NAMES

Prespersion, 75 Urea, Ureophil, Urevert, Aquadrate

IDENTIFICATION NUMBERS

UN No. No hazard label required; CAS No. 57-13-6; OHM-TADS No. 7216943; STCC No. Not required

GRADES & PURITIES

Solid: Technical grade (prills), fertilizer grade (prills or granules), 95 percent and higher urea; 99.7 percent urea contains 46 percent by weight N₂

Liquid: 50-80 percent aqueous solutions

IMMEDIATE CONCERNS

Fire: Not combustible.

Human Health: Relatively nontoxic material.

Environment: Harmful to aquatic life in high concentrations.

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): solid Boiling Point: decomposes before boiling Melting Point: 133°C Flammability: noncombustible, decomposes to ammonia gas above 133°C Specific Gravity: 1.335 (20°C/4°C) Solubility (in water): 51.6 g/100 g (20°C) Behaviour (in water): sinks and mixes; no reaction

ENVIRONMENTAL CONCERNS

Urea is toxic to aquatic life and microorganisms at concentrations above 10 000 mg/L, and to domestic animals at doses above 500 mg/kg.

HUMAN HEALTH

No TLV® or IDLH established.

Exposure Effects

Contact: Causes redness and irritation to skin and eyes.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Notify manufacturer. Stop the flow and contain spill, if safe to do so. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not combustible; most firefighting agents can be used on fires involving urea.

COUNTERMEASURES

Emergency Control Procedures in/on

- Soil: If spilled in solid form, shovel into containers and cover. Construct barriers to contain solutions or divert to impermeable holding area. Remove material by manual or mechanical means. Absorb small amounts of liquid spill with natural or synthetic sorbents, shovel into containers and cover.
- Water: Contain by damming, water diversion or natural barriers. Remove and treat contaminated liquids.

2 [·] PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance

Usual shipping state(s)

Physical state at 15°C, 1 atm Melting point Boiling point Decomposition temperature

Densities

Density

Specific gravity Bulk density

Fire Properties

Flammability 135°C (Kirk-Othmer 1983) Decomposition temperature Decomposition products (Merck 1976)

Other Properties

Molecular weight of pure substance

Constituent components of typical commercial grade

Refractive index

Viscosity

Granular white solid or clear liquid (Sherritt MSDS) Solid: in granule or prill form (Olin PD 1981; Sherritt MSDS) Liquid: aqueous solutions Solid 132.7°C (Olin PD 1981; Ullmann 1975) Decomposes before boiling (Olin PD 1981) 135°C (Kirk-Othmer 1983)

1.3230 g/mL (20°C), 1.147 g/mL (saturated solution at 20°C) (Kirk-Othmer 1983) 1.335 (20°/4°C) (Sherritt MSDS) 0.74 g/cm³ (Kirk-Othmer 1983)

Noncombustible solid (Olin PD 1981) Biuret, ammonia and cyanuric acid

60.06 (CRC 1980)

98 percent urea, 1 percent formaldehyde, 1 percent biuret (H₂NCOHHCONH₂) (Sherritt MSDS)

1.484 (CRC 1980) 1.3535 (5 N solution, 35°C) (Chao 1967)

1.78 mPa·s (46 percent solution, 20°C) (CRC 1980) 1.81 mPa·s (melt at 137°C) (Ullmann 1975) 1.90 mPa-s (saturated solution at 20°C) (Kirk-Othmer 1983)

Vapour pressure

Latent heat of fusion

Latent heat of sublimation Heat of formation Entropy Ionization potential

Heat of solution

Heat capacity constant pressure (Cp)

Diffusivity

pH of aqueous solution

Log₁₀ octanol/water partition coefficient

Dipole moment

Dielectric constant

Solubility

In water

In other common materials

Azeotropes

1.73 kPa (20°C), 5.33 kPa (40°C) (saturated solutions in water) (Kirk-Othmer 1983)

15.1 kJ/mole (at melting point) (Kirk-Othmer 1983; Ullmann 1975)

87.9 kJ/mole (25°C) (Lange's Handbook 1979)

-333.7 kJ/mole (25°C) (Sussex 1977)

105.5 kJ/(mole•K) (Ullmann 1975)

9.7 eV (Debies 1974)

-15.1 kJ/mole (20°C) (Perry 1973) -14.1 kJ/mole (25°C) (Ullmann 1975)

80.5 J/(mole•°C) (solid at 20°C) (Ullmann 1975)
86 J/(mole•°C) (0°C) (Kirk-Othmer 1983)
1.37 x 10⁻⁵ cm²/s (in water 20°C) (Perry 1973)
7.2 (10 percent solution) (Merck 1976)
-1.09 (Hansch and Leo 1979)

4.56, 3.5 (22°C) (Chao 1967) 86.1 (3 N solution at 20°C) (Chao 1967)

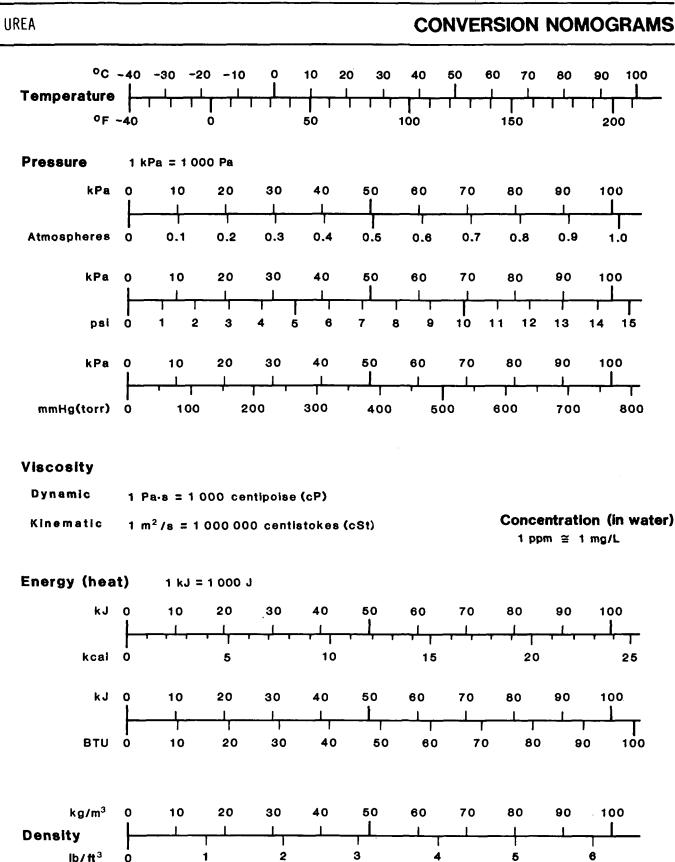
51.6 g/100 g solution (20°C) (Kirk-Othmer 1983)

Very soluble in methanol and ethanol. Soluble in acetic acid and pyrimidine. Insoluble in diethyl ether, chloroform and benzene (CRC 1980)

Solubility in methanol is 22 g/100 g solution; in ethanol, 5.4 g/100 g solution (Ullmann 1975)

Forms azeotrope with water (67.5 percent by mass) which freezes at -11.5°C

TABLE 1



5

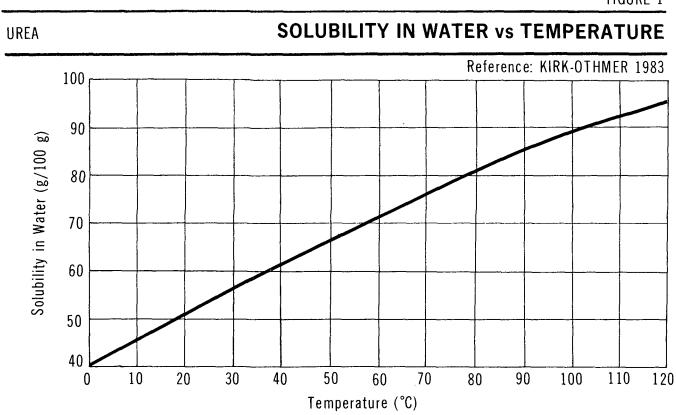
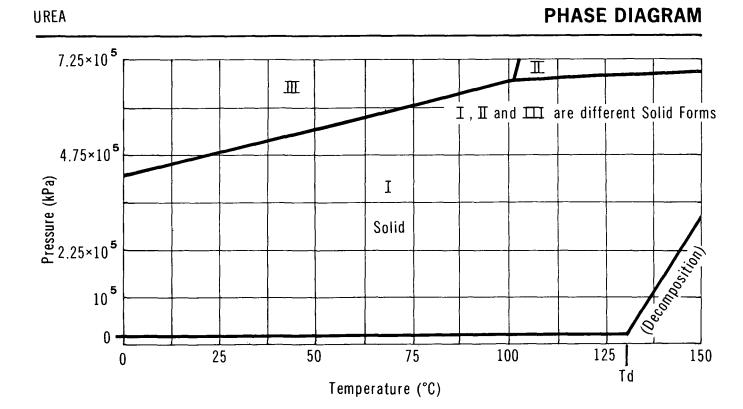


FIGURE 2



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FIGURE 1

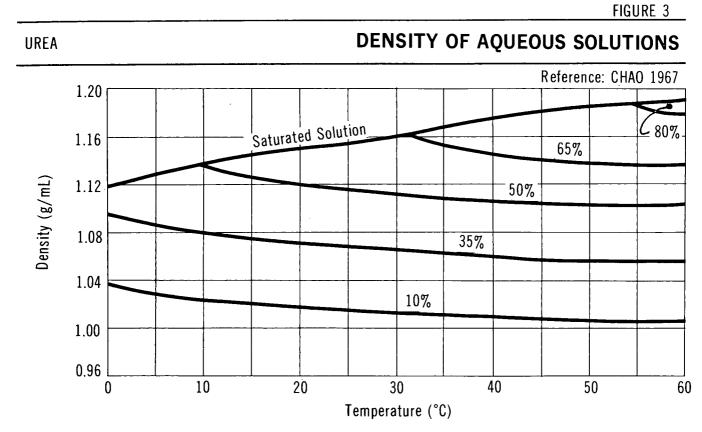
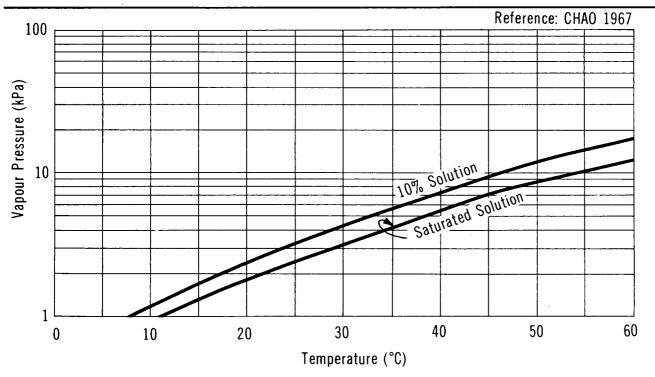


FIGURE 4





UREA

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3

COMMERCE AND PRODUCTION

3.1 Grades, Purities (Sherritt 1982; Cyanamid 1982; CCPA 1984)

Urea is sold as a solid or liquid in a number of grades. Liquid urea is sold in 50-80 percent aqueous solutions. Solid urea (produced in grades containing up to 99 percent urea) is sold in the following grades: regular fertilizer grade, granulated or prilled urea containing less than 1.5 percent biuret; special grade, prilled, for special fertilizer applications, containing less than 0.3 percent biuret; technical grade, prilled; and prilled or microprilled feed grade. <u>Note</u>: Most solid grades contain 0.5-1.0 percent biuret unless otherwise noted. Higher amounts of biuret (>2 percent) are detrimental to plant growth. Some urea may contain 0-1 percent formaldehyde.

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

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

Canadian Fertilizers P.O. Box 1300 Medicine Hat, Alberta T1A 7N1 (403) 527-8887

C-I-L. Inc. P.O. Box 200, Station A 90 Sheppard Avenue East North York, Ontario M2N 6H2 (416) 226-6110

Cominco 200 Granville Street Vancouver, British Columbia V6C 2R2 (604) 682-0611

Cyanamid Canada Inc. 2255 Sheppard Avenue East Willowdale, Ontario M2J 4Y5 (416) 498-9405 Nitrochem Inc. 2055 Peel Street, Suite 800 Montreal, Quebec H3B 2X8 (514) 849-9222

Sherritt Gordon Mines Ltd. Box 28, Commerce Court West Toronto, Ontario M5L 1B1 (416) 363-9241

Simplot Chemical Co. Ltd. P.O. Box 940 Brandon, Manitoba R7A 6A1 (204) 728-5701

3.3 Other Suppliers (CBG 1980; Corpus 1983; Scott 1979)

Arliss Chemical Co. Inc. 325 Hymus Blvd. Pointe-Claire, Quebec H9R 1G8 (514) 694-2170

BASF Canada Ltd. 5850 Cote de Liesse Montreal, Quebec H4T 1C1 (514) 341-5411

Canada Colours and Chemicals Ltd. 80 Scarsdale Road Don Mills, Ontario M3B 2R7 (416) 924-6831

Coté Chemicals Inc. 111 Bombardier Park Chateauguay Centre, Quebec J6J 3X0 (514) 691-6260

Esso Chemical Canada Division of Imperial Oil Ltd. 2300 Yonge Street Toronto, Ontario M5W 1K3 (416) 488-6600

Harrison & Crosfield (Canada) Ltd. 4 Banigan Drive Toronto, Ontario M4H 1G1 (416) 425-6500 International Chemical Canada Ltd. P.O. Box 385 Brampton, Ontario L6V 2L3 (416) 453-4234

Mallinckrodt Canada Inc. 600 Delmar Avenue Pointe-Claire, Quebec H9W 1E6 (514) 695-1220

Nitrochem Inc. 2055 Peel Street Suite 800 Montreal, Quebec H3B 2X8 (514) 849-9222

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

United Co-operatives of Ontario (Captive) 151 City Centre Drive Mississauga, Ontario L5A 3A4 (416) 270-3560

3.4 Major Transportation Routes

Current Canadian production of urea is located primarily in Alberta, at Medicine Hat, Carseland, Fort Saskatchewan and Calgary. Other production facilities are in Ontario, at Courtright, Maitland and Niagara Falls, and in Manitoba, at Brandon. The product is shipped by box cars, tank cars, tank trucks or flatbed trucks.

3.5 Production Levels (Corpus 1983)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1982)
Canadian Fertilizers, Medicine Hat, Alta.	, , , , , , , , , , , , , , , , , , , 	435
C-I-L, Courtright, Ont.		160
Cominco, Calgary, Alta.		70
Cominco, Carseland, Alta.		435
Cyanamid Canada, Niagara Falls, Ont.	90	
Nitrochem, Maitland, Ont.	45*	
Sherritt Gordon Mines, Ft. Saskatchewan,	80	
Simplot Chemical, Brandon, Man.		142
	TOTAL	1457
Domestic Production (1982)		1230.5
Imports (1982)		101
	TOTAL SUPPLY	1331.5

* Plant moth-balled in 1983.

C-I-L is planning to expand its plant in Courtright, Ontario, by 134 kt/yr (CCP 1982b). Sherritt Gordon (Fort Saskatchewan, Alberta) is expanding its urea capacity by 220 kt/yr; Simplot (Brandon, Manitoba) is expanding by 115 kt/yr (Corpus 1983).

3.6 Manufacture of Urea (Kirk-Othmer 1983; Sullivan 1982; FKC 1975)

3.6.1 General. Urea is made by the reaction of anhydrous ammonia and carbon dioxide to form ammonium carbamate, and the decomposition of the latter to urea.

3.6.2 Manufacturing Process. An excess of liquid ammonia and gaseous carbon dioxide (usually at a ratio of 2.5:1) are fed into a reactor with a small amount of water:

 $2NH_3 + CO_2 \rightarrow NH_4CO_2NH_2 \rightarrow NH_2CONH_2 + H_2O$ (ammonium carbamate) (urea)

The reaction is conducted at a pressure of about 20 000 kPa and a temperature of 180-200°C, in the presence of a metal catalyst. The conversion to ammonium carbamate is nearly quantitative; conversion to urea is in the 50-70 percent range, depending on the process.

The reaction mixture is then conducted to a series of decomposers where the pressure is reduced and unconverted ammonium carbamate is decomposed by heat. The resulting ammonia and carbon dioxide, as well as the excess of ammonia originally charged, are ultimately recycled.

Urea solids are produced by flash distillation or vacuum crystallization of water from the urea solution; prills are formed by dropping molten urea down a spray tower. Anti-caking ingredients may be added at this stage to facilitate handling and storage.

3.7 Major Uses in Canada (Corpus 1983)

Urea is used in direct fertilization, forest fertilization, nitrogen (and nitrogenphosphate) solutions, fertilizer mixtures, animal feeds, and U-F resins. In 1982, 44 percent of domestic production was exported, 37 percent was used for direct fertilization and 8 percent was used for nitrogen solutions.

3.8 Major Buyers in Canada (Corpus 1983; CCPA 1984)

Agricultural Chemicals, London, Ont. Borden Chemical, Toronto, North Bay, Ont. Canada Packers, Toronto, Ont. Coopérative Fédérée du Québec, Montréal, Qué. William Houde, Laprairie, Que. MacMillan Bloedel, Vancouver, B.C. Monsanto Canada, LaSalle, Que. Nitrochem Inc., Montreal, Que. Northwood Pulp, Prince George, B.C. Nutrite Inc., Toronto, Ont. Pacific Logging, Victoria, B.C. Perkins Adhesives, Valleyfield, Que. Reichhold, North Bay, Ont. St. Regis Alberta, Hinton, Alta. United Cooperatives of Ontario, Mississauga, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. A large portion of the material is shipped as a solid by rail or truck, or as a solution by rail.

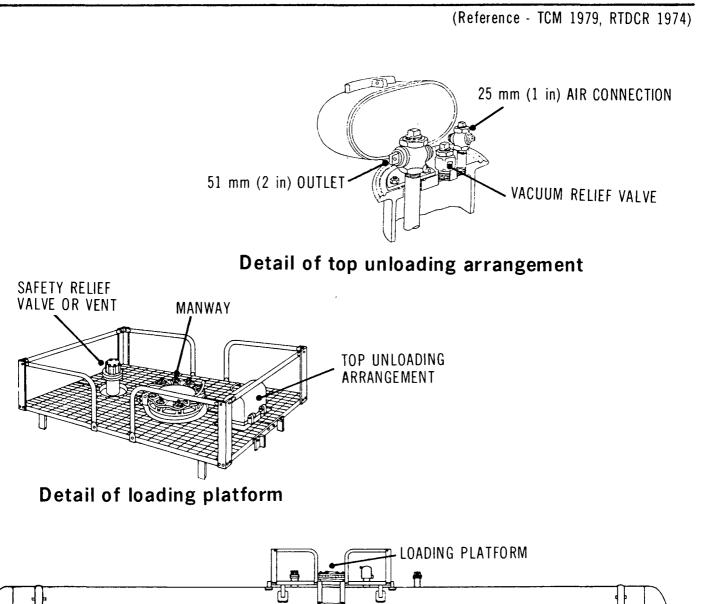
4.1.1.1 Railway cars. Railway tank cars used for transporting solutions are not regulated. Commonly used tank cars are described in Table 2. As indicated in Table 2, tankers may be unloaded from top or bottom depending on the class of car selected. Cars may be unloaded from the top or bottom by pump or by gravity from the bottom (PC 1982). A typical 111A60W1 tank car is illustrated in Figure 5; details associated with this car are given in Table 3.

CTC/DOT* Specification Number	Description
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum out- age. Gauging device. Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi). Test pressure 414 kPa (60 psi). Urea resins only.
111A60W1 (IL)	Same as 111A60W1 except interior-lined for urea solutions.
111A60ALW1	Aluminum fusion-welded tank without dome. Uninsulated or insulated. 2% minimum out- age. Gauging device. Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi). Bottom outlet or washout optional. Test pressure 414 kPa (60 psi). For urea solutions and resins.
111A100W6	Alloy (stainless) steel fusion-welded tank without dome. Insulated or uninsulated. 2% minimum outage. Gauging device. Safety valve (518 kPa) (75 psi) or safety vent (690 kPa) (100 psi). Bottom outlet or wash- out optional. Test pressure 690 kPa (100 psi). Urea resins only.

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

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

RAILWAY TANK CAR - CLASS 111A60W1



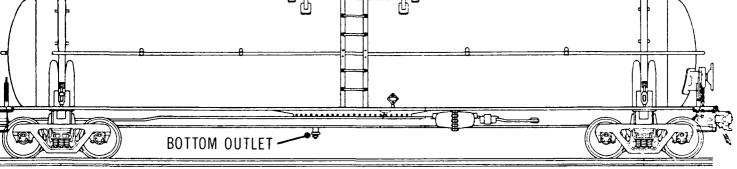


Illustration of tank car layout

UREA

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A60W1 (TCM 1979; RTDCR 1974)

	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 38 900 kg 119 000 kg	(20 000 gal.) (85 800 lb.) (263 000 lb.)
Tank						
Material Thickness Inside diameter Test pressure Burst pressure	steel 11.1 mm 2.60 m 414 kPa 1640 kPa	(7/16 in.) (102 in.) (60 psi) (240 psi)	steel 11.1 mm 2.62 m 414 kPa 1640 kPa	(7/16 in.) (103 in.) (60 psi) (240 psi)	steel 11.1 mm 2.74 414 kPa 1640 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 to 3 m 1.5 to 2 m	(57 ft.) (53 ft.) (42 ft.) (12 ft.) (15 ft.) (127 in.) (8 to 10 ft.) (5 to 6 ft.)	17 m 16 m 13 m 4 m 5 m 3.2 m 2 to 3 m 1.5 to 2 m	(57 ft.) (53 ft.) (42 ft.) (12 ft.) (15 ft.) (127 in.) (8 to 10 ft.) (5 to 6 ft.)	18 m 17 m 14 m 4 m 5 m 3.2 m 2 to 3 m 1.5 to 2 m	(60 ft.) (57 ft.) (45 ft.) (13 ft.) (15 ft.) (127 in.) (8 to 10 ft.) (5 to 6 ft.)
Loading/Unloading Fixtures						
Top Unloading						
Unloading connection Manway/fill hole Air connection	51 mm 203 to 356 mm 25 to 51 mm	(2 in.) (8 to 14 in.) (1 to 2 in.)	51 mm 203 to 356 mm 25 to 51 mm	(2 in.) (8 to 14 in.) (1 to 2 in.)	51 mm 203 to 356 mm 25 to 51 mm	(2 in.) (8 to 14 in.) (1 to 2 in.)
Bottom Unloading						
Bottom outlet	102 to 152 mm	(4 to 6 in.)	102 to 152 mm	(4 to 6 in.)	102 to 152 mm	(4 to 6 in.)
Safety Devices	Safety vent or	valve				
Dome	None					
Insulation	Optional					

•

Solid prill and granular material is transported in covered bulk hopper cars and box cars in bagged form. Hopper cars are gravity or pneumatically unloaded. Capacities vary from 45 to 90 tonnes (PC 1982). Typical hopper cars are illustrated in Figure 6 and described in Table 4. "Cylindrical" hopper cars with specifications similar to the latter are also frequently used.

4.1.1.2 Tank motor vehicles. Solid prill and granular material is transported in bulk form in dump trucks or in pneumatic type trucks in capacities of 18 to 45 tonnes. In bagged form, flatbed trucks are utilized (PC 1982).

Urea solutions are not specifically regulated, but MC311 and MC312 carriers are generally used. Both classes are covered under the Transport Canada TC312 specifications. Such specifications require that cargo tanks unloaded by pressure in excess of 104 kPa (15 psi) be designed and constructed in accordance with the ASME Code (TDGC 1980). Capacities of highway tankers transporting urea solutions vary from 18 to 32 tonnes. Insulated stainless steel tankers usually transport 50-80 percent aqueous solutions (PC 1982).

4.1.2 Packaging. In addition to bulk shipments, urea in prilled and granulated form is also shipped in drums, paper bags and plastic bags (PC 1982).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Two means of off-loading urea solution rail cars are used, top off-loading and bottom off-loading.

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

- Remove the protective housing from the discharge value at the top of the car and connect the 51 mm (2 in.) unloading line.
- Off-load the tanker by pumping.

Proceed with bottom off-loading as indicated below:

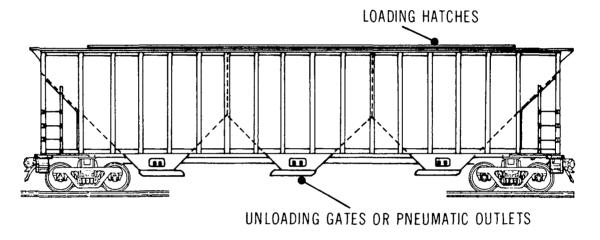
- Connect the unloading line to a 152 mm (6 in.) bottom outlet and open the inside bottom valve by turning the valve handle at the top of the car.
- Off-load the car by gravity or pump.

Prior to off-loading granular and prilled urea, certain chemicals such as urea formaldehyde are often added to control dust (Sherritt MSDS 1978).

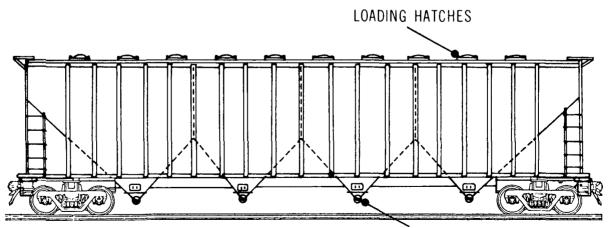
4.2.2 Specifications and Materials for Off-loading Equipment. Fully annealed Schedule 40 carbon steel mechanical tubing made to ASTM Specification A53 and then

COVERED HOPPER CARS - AAR CLASS LO

(Reference - CLC 1974, AAR 1983)







UNLOADING GATES OR PNEUMATIC OUTLETS

Typical 4 - Compartment Hopper Car

Hopper Car Size (cu. ft.) 5800 4700 Description 164 m³ (5800 cu. ft.) Nominal capacity 86 000 kg (190 000 lb.) Weight capacity

Weight capacity Car weight - empty Car weight - max.	86 000 kg (190 000 lb.) 45 000 kg (100 000 lb.) 119 000 kg (263 000 lb.)	
Hoppers/Compartments		
Number Material Inside length (typical) Inside width (typical) Spacing between outlets Slope angle	4 steel 410 cm (160 in.) 300 cm (118 in.) 4 m (13 ft.) 40 to 45°	3 steel 460 cm (180 in.) 300 cm (118 in.) 5 m (15 ft.) 40 to 45°
Approximate Dimensions		
Coupled length Length over strikers Length of truck centres Clearance height Height to top of running board Overall width Inside length	21 m (68 ft.) 20 m (65 ft.) 16 m (54 ft.) 5 m (15 ft.) 3.1 m (123 in.) 19 m (63 ft.)	<pre>18 m (60 ft.) 17 m (57 ft.) 14 m (46 ft.) 5 m (15 ft.) 4 m (14 ft.) 3.2 m (126 in.) 17 m (55 ft.)</pre>

Loading/Unloading Fixtures

Loading Hatches:	Cars typically equipped with 4 to 12 loading hatches. Typical dimensions of these are 36 to 61 cm (14 to 24 in.) in diameter or square dimensions.
Unloading Fixtures:	Equipped with unloading gates at bottom of 36 to 61 cm (14 to 24 in.) square and/or pneumatic unloading connections of 10 to 20 cm (4 to 8 in.) in diameter.

lined with polyvinylidene chloride (Saran) is recommended for urea solutions at medium temperatures (DPLP 1972). Plain carbon steel pipes and fittings may be used at normal temperatures (PC 1982). Flanged joints of compatible material should be used. The unloading line is usually 51 mm (2 in.) pipe, to suit standard discharge fittings on rail cars.

TABLE 4

Overall

TYPICAL RAILWAY HOPPER CAR SPECIFICATIONS - AAR CLASS LO (CLC 1974)

133 m³ (4700 cu. ft.)

Flexible bellows-type expansion joints may be used for the flexible sections of the unloading line. They are manufactured with ASA ductile iron flanges with expansion member molded from tetrafluoroethylene resin (Dow PPS 1972).

Diaphragm valves of cast iron bodies lined with chlorinated polyether or polyvinylidene chloride resin will serve adequately (DPLV 1972). Chlorosulphonated polyethylene resin is an adequate gasket material in this service (DPLP 1972).

An all-iron centrifugal pump, close-coupled, is suitable in this service. Stainless steel or Monel are recommended (Cyanamid MSDS 1976).

For handling granular and prilled material, normal solids handling equipment is used (Sherritt MSDS 1978).

4.3 Compatibility with Materials of Construction

The compatibility of urea solutions with materials of construction is indicated in Table 5. The unbracketed abbreviations are described in Table 6. The rating system 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		
		ai .			Not
Application	Conc.	Temp. (°C)	Recommended	Conditional	Recommended
1. Pipes and Fittings	Most	23	PE* (DPPED 1967)		
		52	PVDC (DCRG 1978)		
		60	PVC I PVC II (DPPED 1967)		
		93	PP (DCRG 1978)		

				Material of Construction		
		Chemical				Not
Ap	plication	Conc.	Temp. (°C)	Recommended	Conditional	Recommended
1.	Pipes and Fittings (Cont'd)		121	PVDF Chlorinated Polyether (DCRG 1978)		
·			To operat- ing limit of material	PVC I (MWPP 1978		
		Solid product	Most	CS (Cyanamid MSDS 1976)		ABS, PE (MWPP 1978)
2.	Valves	Most	23	Chlorinated Polyether PVDC SS 316, SS 317 (Cyanamid MSDS 1976)		
3.	Pumps	Most	Most	Iron SS (Cyanamid MSDS 1976)		
4.	Storage	Most	Most	CS, SS (PC 1982)		
5.	Others	Up to 10% or 33%	60	PE, PP POM, NR NBR, IIR EPDM, CR FPM, CSM (GF)	uPVC (GF)	
			60	PVC (TPS 1978)		
			82	PP (TPS 1978)		
			85	CPVC (TPS 1978)		
			121	PVDF (TPS 1978) SBR (GPP)		
		10 to 50%	24 to 100	Glass (CDS 1967)		

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

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

Abbreviation	Material of Construction		
ABS	Acrylonitrile Butadiene Styrene		
	Aluminum		
	Cast Iron		
	Chlorinated Polyether		
CPVC	Chlorinated Polyvinyl Chloride		
CR	Polychloroprene (Neoprene) Rubber		
CS	Carbon Steel		
CSM	Chlorosulphonated Polyethylene (Hypalon)		
EPDM	Ethylene Propylene Rubber		
FPM	Fluorine Rubber (Viton)		
	Glass		
	Iron		
IIR	Isobutylene/Isoprene (Butyl) Rubber		
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber		
NR	Natural Rubber		
	Nickel-Copper Alloy (Monel)		
PE	Polyethylene		
РОМ	Polyoxymethylene		
РР	Polypropylene		
PVC (followed by grade if any)	Polyvinyl Chloride		
PVDC	Polyvinylidene Chloride		
PVDF	Polyvinylidene Fluoride		
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber		
SS (followed by grade)	Stainless Steel		
	Tetrafluoroethylene		
uPVC	Unplasticized Polyvinyl Chloride		

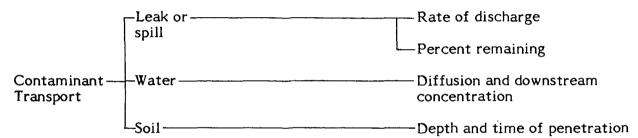
TABLE 6MATERIALS OF CONSTRUCTION

5 CONTAMINANT TRANSPORT

5.1 General Summary

Urea is transported as a solid, in granule or prill form, in covered hopper cars, or as an aqueous solution in tankers. When spilled in water, all forms will dissolve rapidly. When spilled on soil, the liquid form will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Transport of urea toward the water table may be an environmental concern. Because urea is essentially nonvolatile, dispersion in air is not a problem.

Factors considered for the transport of a urea spill in water and soil are shown below:



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

5.2 Leak Nomograms

5.2.1 Introduction. Urea is transported as solid crystals or pellets or as an aqueous solution. In aqueous form, urea is commonly transported in railway tank cars. While the capacities of the tank cars vary widely, one tank car 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 manuals to allow for comparison between different substances.

If a tank car loaded with dilute aqueous solution is punctured on the bottom, all of the contents will drain out by gravity. Higher concentrations of urea solution are highly viscous or solid at normal temperatures and will not drain by gravity unless the temperature is elevated.

The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the low volatility of urea solution and the fact that tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

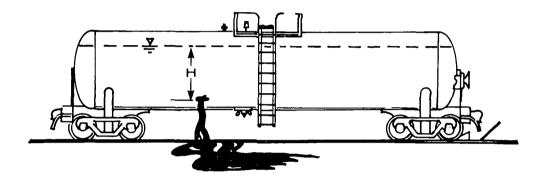


FIGURE 7 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

5.2.2 Nomograms.

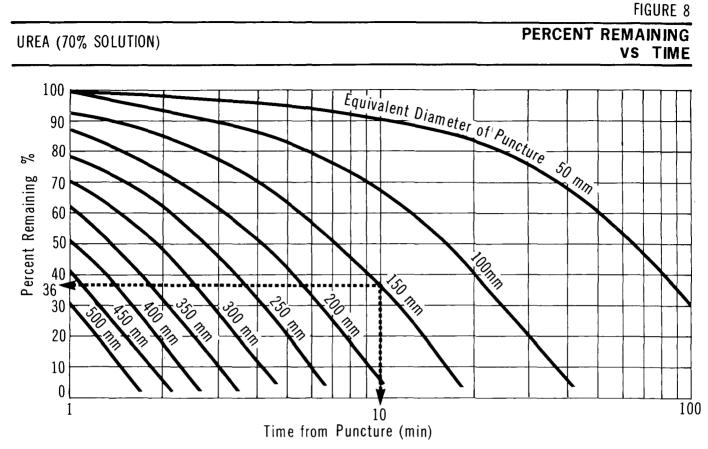
5.2.2.1 Figure 8: Percent remaining versus time. Figure 8 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular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

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

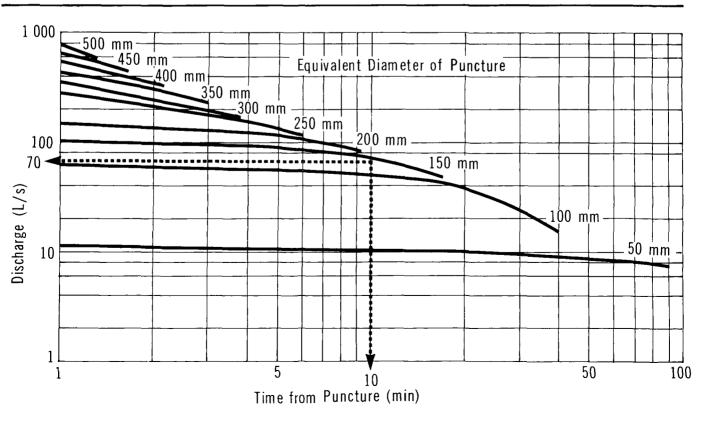
The standard tank car filled with a 70 percent aqueous solution of urea has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?



UREA (70% SOLUTION)

FIGURE 9

DISCHARGE RATE VS TIME



23

Solution to Problem A

- . Use Figure 8
- . With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28 800 L $\,$

ii) Problem B

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

Solution to Problem B

- . Use Figure 9
- . With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

Because urea is nonvolatile in foreseeable spill circumstances, there is no significant potential for dispersion in air.

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, urea will dissolve rapidly. 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.

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

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time. **5.4.2** Nomograms. The following nomograms are presented to calculate pollutant concentrations in non-tidal rivers and in lakes (still water).

Non-tidal Rivers

Figure 11:	time versus distance for a range of average stream velocities		
Figure 12:	hydraulic radius versus channel width for a range of stream depths		
Figure 13:	diffusion coefficient versus hydraulic radius for a range of average stream velocities		
Figure 14:	alpha* versus diffusion coefficient for various time intervals		
Figure 15:	alpha versus delta* for a range of spill sizes		
Figure 16:	maximum concentration versus delta for a range of river cross-sectional areas		

Lakes or Still Water Bodies

- Figure 17: volume versus radius for the hazard zone for a range of lake depths
- Figure 18: average concentration versus volume for the hazard zone for a range of spill sizes.

The flowchart in Figure 10 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 11 through 18) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

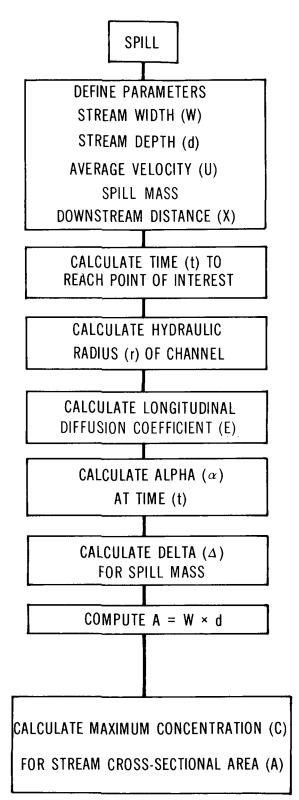
Figure 11: Time versus distance. Figure 11 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest, at some distance (X) downstream of the spill, can be readily obtained from Figure 11.

Figure 12: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 12 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

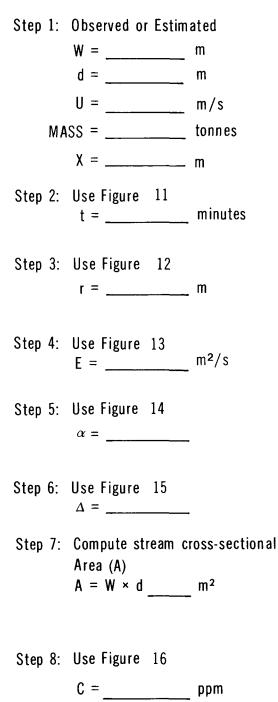
^{*} Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

FIGURE 10

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS



UREA

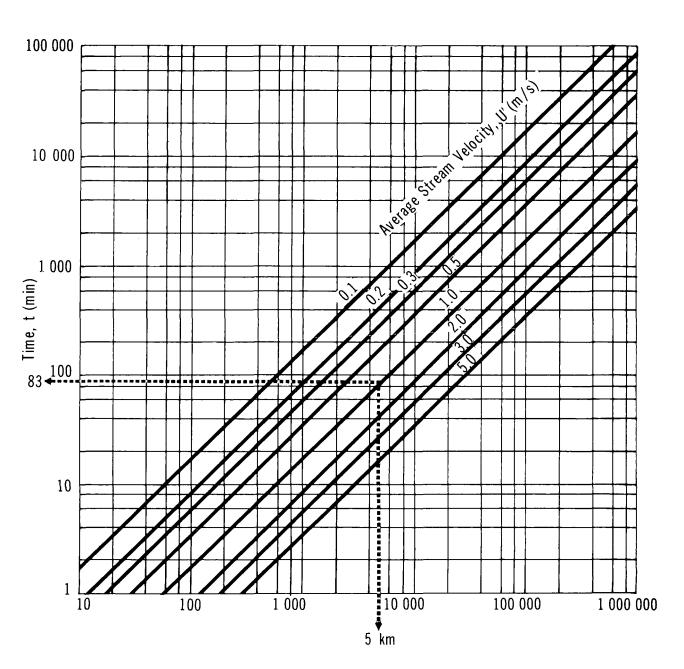


26

FIGURE 11

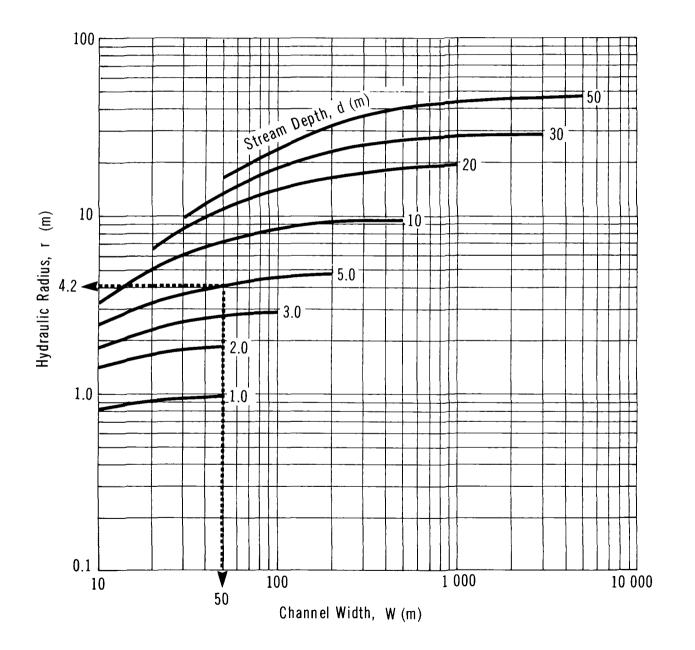


TIME vs DISTANCE



Distance, X (m)

•



UREA

HYDRAULIC RADIUS VS CHANNEL WIDTH

FIGURE 12

Figure 13: Diffusion coefficient versus hydraulic radius. Figure 13 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 12 and the average stream velocity (U).

Figure 14: Alpha versus diffusion coefficient. Figure 14 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 15: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 15 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 16: Maximum concentration versus delta. Figure 16 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 16 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.2.2 Nomograms for lakes or still water bodies.

Figure 17: 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 17. The radius (r) represents the distance from the spill to the point of interest.

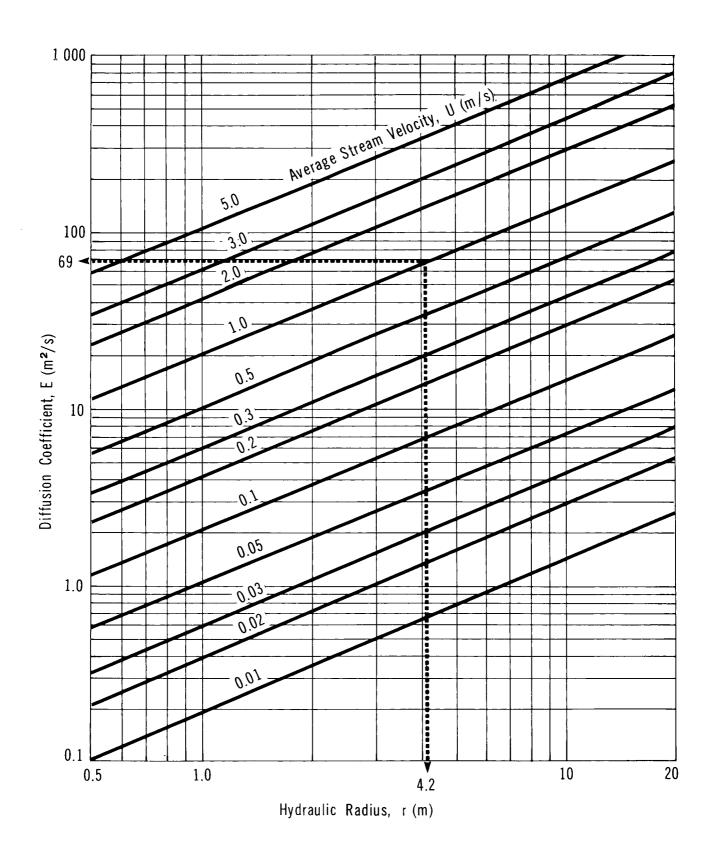
Figure 18: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 18 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal rivers. A 10 tonne spill of 60 percent urea solution has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

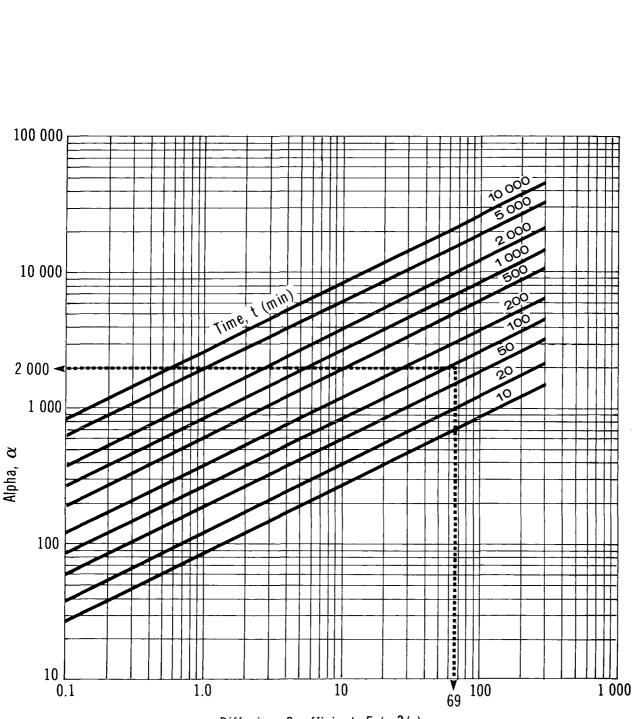
FIGURE 13

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS



UREA

ALPHA vs DIFFUSION COEFFICIENT



Diffusion Coefficient, E (m^2/s)

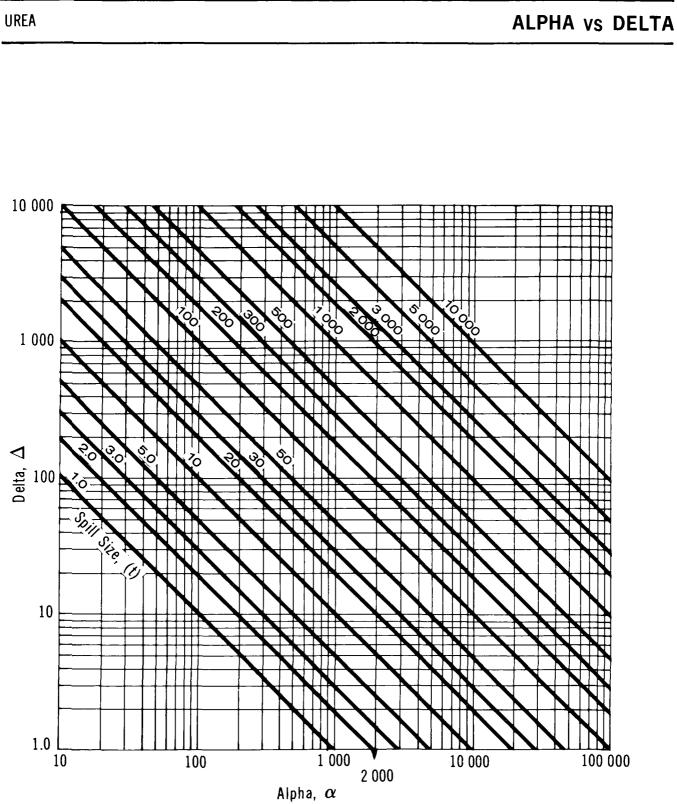
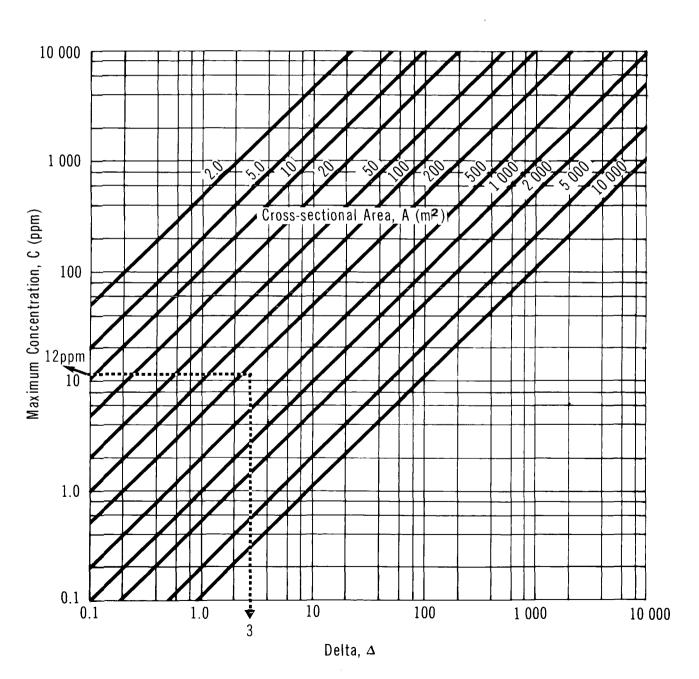
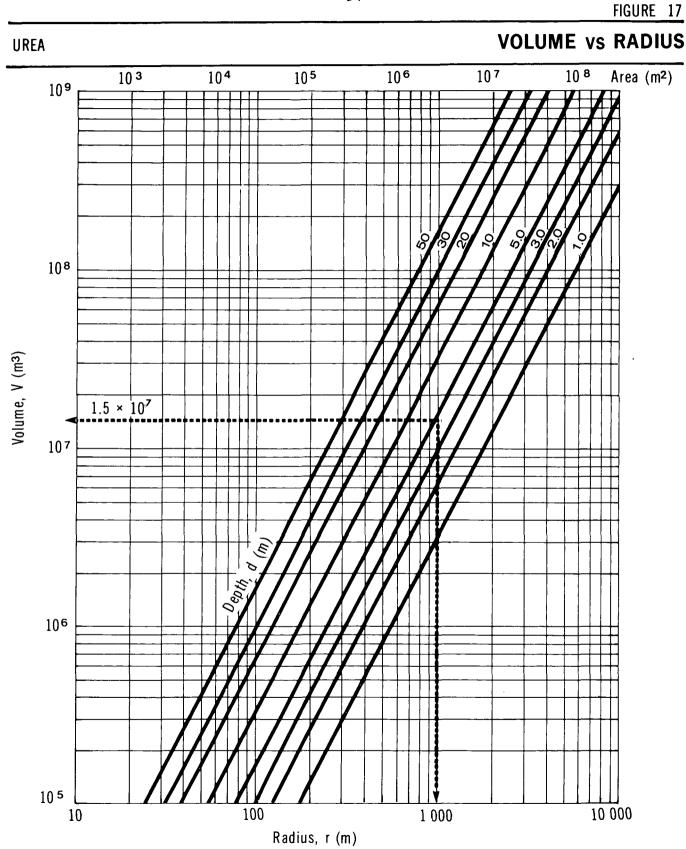
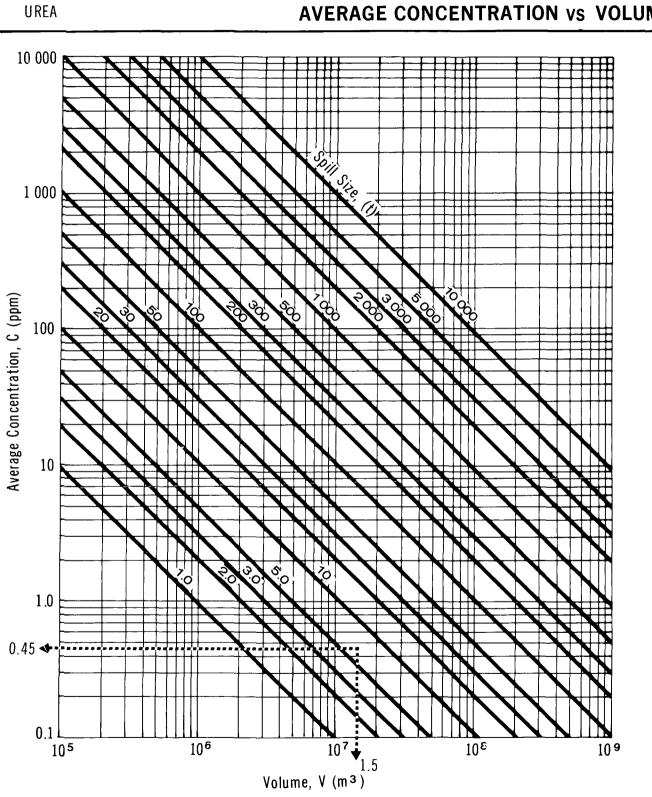


FIGURE 15

MAXIMUM CONCENTRATION vs DELTA







AVERAGE CONCENTRATION vs VOLUME

Solution

Step 1:	Define parameters
	• W = 50 m
	• d = 5 m
	• U = 1 m/s
	 spill mass = 10 tonnes of 60 percent urea solution contains the equivalent of 6 tonnes of urea
Step 2:	Calculate the time to reach the point of interest
	• Use Figure 11
	• With $X = 5000 \text{ m}$ and $U = 1 \text{ m/s}$, $t = 83 \text{ min}$
Step 3:	Calculate the hydraulic radius (r)
	• Use Figure 12
	• With $W = 50 \text{ m}$ and $d = 5 \text{ m}$, $r = 4.2 \text{ m}$
Step 4:	Calculate the longitudinal diffusion coefficient (E)
	• Use Figure 13
	• With $r = 4.2 \text{ m}$ and $U = 1 \text{ m/s}$, $E = 69 \text{ m}^2/\text{s}$
Step 5:	Calculate alpha (α)
	• Use Figure 14
	• With E = 69 m ² /s and t = 83 min, α = 2000
Step 6:	Calculate delta (Δ)
	• Use Figure 15
	. With alpha (α) = 2000 and spill mass = 6 tonnes, delta (Δ) = 3
Step 7:	Compute the stream cross-sectional area (A)
	• $A = W \times d = 50 \times 5 = 250 \text{ m}^2$
Step 8:	Calculate the maximum concentration (C) at the point of interest
	• Use Figure 16
	• With $\Delta = 3$ and $A = 250 \text{ m}^2$, $C = 12 \text{ ppm}$

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 10 tonne spill of 60 percent urea solution has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

- Step 1: Define parameters
 - . d = 5 m
 - . r = 1000 m
 - spill mass = 6 tonnes (equivalent)
- Step 2: Determine the volume of water available for dilution
 - . Use Figure 17
 - . With r = 1000 m, d = 5 m, the volume is approximately $1.5 \times 10^7 \text{ m}^3$
- Step 3: Determine the average concentration
 - . Use Figure 18
 - . With V = $1.5 \times 10^7 \text{ m}^3$ and spill mass = 6 tonnes, the average concentration is 0.45 ppm

5.5 Subsurface Behaviour: Penetration into Soil

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

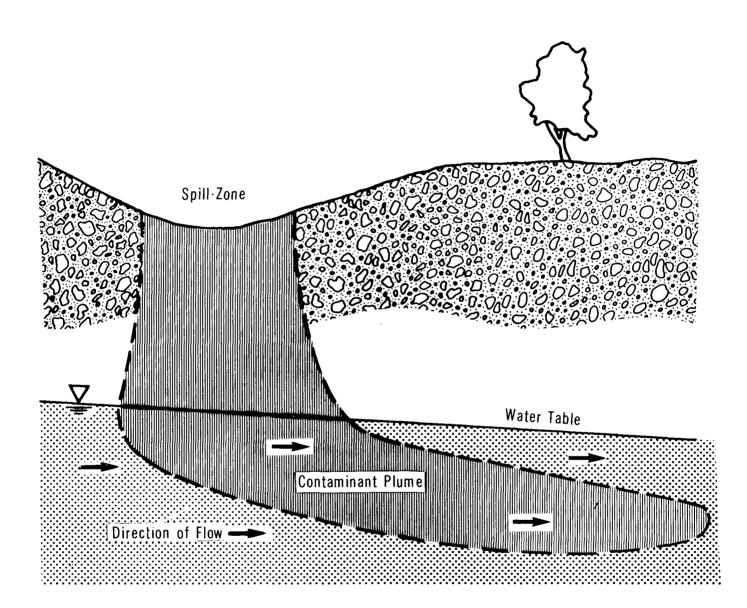
Some urea is conveyed as an aqueous solution although the solid form is more common. When the solid is spilled, only a limited groundwater contamination hazard exists if the soil is dry and if no precipitation falls prior to cleanup. However, if the solution is spilled, or if precipitation or other forms of moisture are present, groundwater contamination can be expected.

Since urea is very soluble (51.6 g/100 g solution at 20°C), concentrated solutions can infiltrate the soil. Some interaction between urea and the soil will occur. However, much of the urea exchanged ions will migrate downward through the soil.

If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical may run off into surface water. For this work, the soils have been assumed to be at field capacity. This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with diffusion and dispersion serving to reduce the acid concentration somewhat. This is shown schematically in Figure 19.

SCHEMATIC SOIL TRANSPORT



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

UREA

5.5.2 Equations Describing Urea Solution Movement into Soil. The equations and assumptions used to describe contaminant movement in solutions 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 Urea Solution in Soil. The saturated hydraulic conductivity (K_0) , in m/s, is given by:

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

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 fluids involved are urea solution (20 percent by weight) and water. The water calculations represent the extreme as the solution is diluted.

Property	Urea (20% by Wt.) 20°C	Water 20°C
Mass density (ρ), kg/m ³	1053	998
Absolute viscosity (µ), Pa•s	1.18 x 10-3	1.0×10^{-3}
Saturated hydraulic conductivity (K ₀), m/s	(0.87 x 10 ⁷)k	(0.98 x 10 ⁷)k

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

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

5.5.5 Penetration Nomograms. Nomograms for the penetration of urea solutions into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p .

A flowchart for the use of the nomograms is presented in Figure 20. The nomograms are presented as Figures 21, 22 and 23. The water lines on the nomograms represent the maximum penetration of water at 20°C in time t_p . It is a limiting condition as urea becomes diluted with water.

5.5.6 Sample Calculation. A 20 tonne spill of urea has taken place on a silty sand soil. The temperature is 20°C; the spill radius is 8.6 m. A rainfall has occurred. Estimate the depth of urea penetration 8 days after the rain.

Solution

Step 1:	Define parameters
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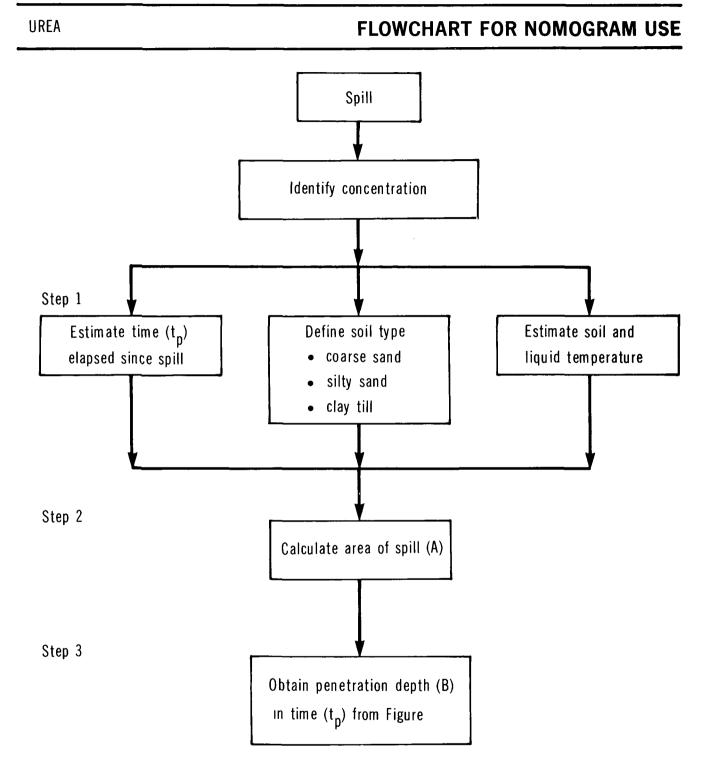
- Mass spilled = 20 000 kg (20 tonnes)
- . T = 20°C
- r = 8.6 m
- Soil = silty sand
- . Groundwater table depth (d) = 13 m
- Time since spill (t_D) = 8 days
- Step 2: Calculate the area of spill
 - $A = \pi r^2 = 232 m^2$

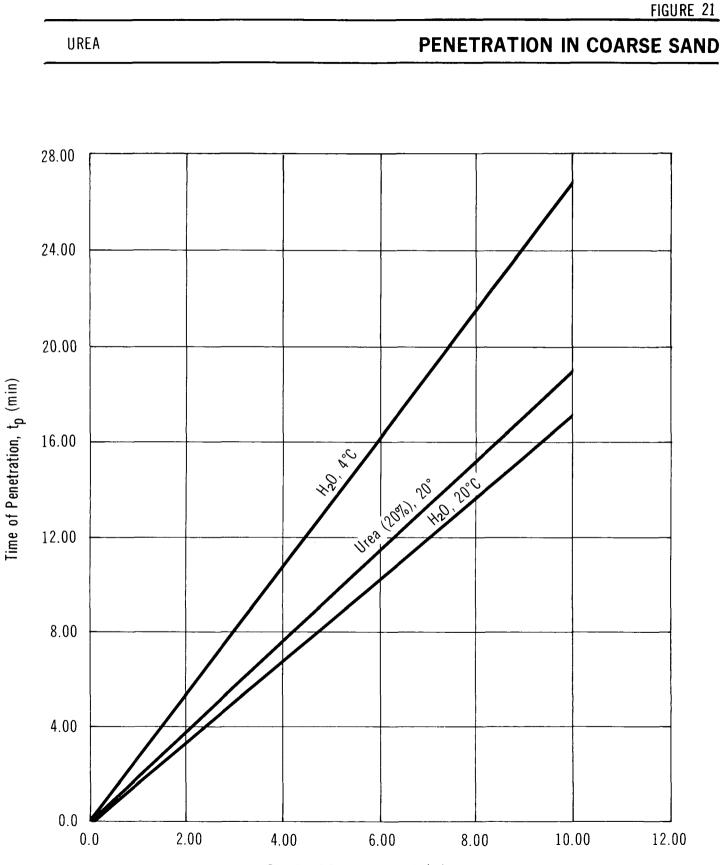
Step 3: Estimate the depth of penetration (B) at time (t_p)

For silty sand and $t_{D} = 8$ days, the penetration range is

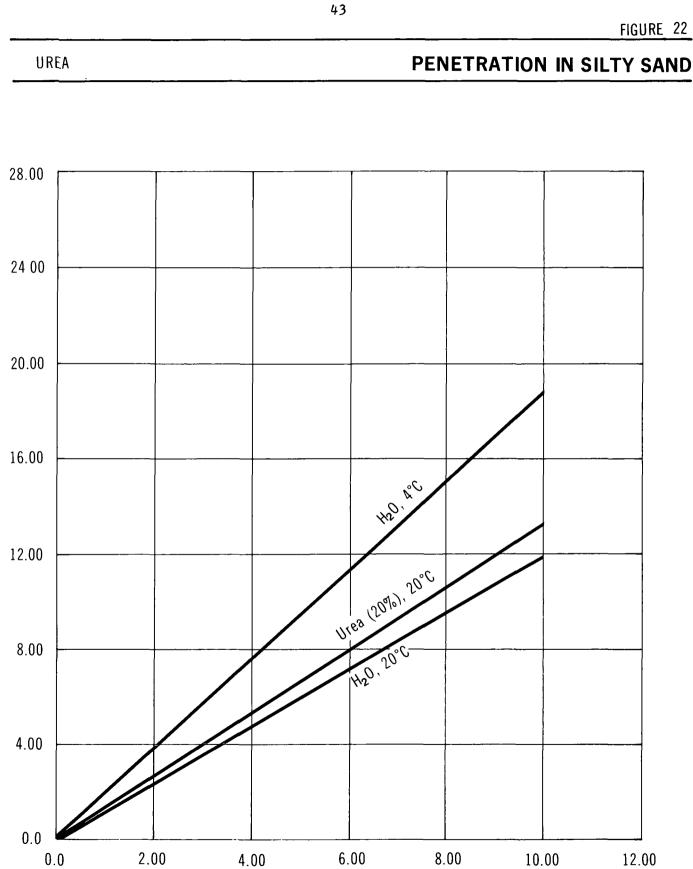
20% by wt.	Dilute	Dilute (Water, worst case)		
6.0 m		6.7 m		

Groundwater table has not been reached at this point





Depth of Penetration, B (m)

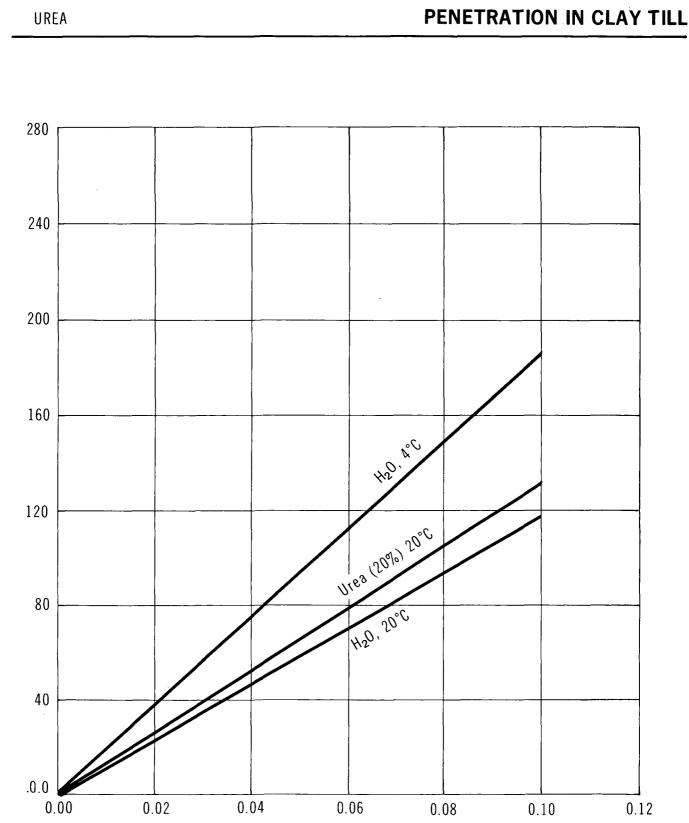


Depth of Penetration, B (m)

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Time of Penetration, t_p (days)



Depth of Penetration, B (m)

Time of Penetration, t_p (days)

FIGURE 23

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Drinking Water. The maximum allowable concentration of urea in Class I waters for drinking is 10 mg/L (Verschueren 1984). This is reportedly the maximum concentration producing no organoleptic effects in man (WQCDB-1 1970).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Urea has been assigned a TL_m 96 of over 1000 ppm (RTECS 1979).

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxic	ity Tests				
17.1	24	Minnows	not noticeable	stabilized tap water	WQC 1963
16 000 to 30 000	24	Creek chub	critical range be- low which 4 test fish lived 24 h and above which all died	Detroit River	Gillette 1952
Microorga	nisms				
>10 000	16	Bacteria (Pseudo- monas putida)	toxic, in- hibit cell multipli- cation	double-dis- tilled water, 25°C	Bringman 1980
>10 000	7 days	Green algae (Scenedesmus qua- dricauda)	toxicity threshold	double-dis- tilled water, 27°C, 50% relative humidity	Bringman 1980
29	72	Protozoa (Entosiphon sulcatum)	toxicity threshold	double-dis- tilled water, 25°C	Bringman 1980

6.3 Mammalian Toxicology

6.3.1 Toxicity.

Conc. (mg/L)	Species	Result	Reference
500	Sheep	LD ₁₀₀ ; mean survival time: 165 min	Edjtehadi 1978
600	Sheep	LD ₁₀₀ ; mean survival time: 109 min	Edjtehadi 1978
750	Sheep	LD ₁₀₀ ; mean survival time: 60 min	Edjtehadi 1978
450 g	Ponies	80% death; oral administration	Clarke 1975
50 g	Goats	80% death within 30 min; oral	Clarke 1975
100 g/day	Sheep	consumption; conc. of urea cannot exceed 6%	Clarke 1975
2000	Adult sheep	continuous convulsions after 165 min	Clarke 1975
2000	Lambs	toxic: died in 90 to 200 min	Clarke 1975
4 <i>5</i> 0	Cattle	toxic dose; given first time	Clarke 1975
50 g	Cattle	poisoning (min. first dose)	Clarke 1975
100 to 200 g	Cattle	increasing dose at various time; no ill effect	Clarke 1975

Cattle quickly develop tolerance to urea doses, but such tolerance is readily lost if urea is withheld a few days. Poisoning of cattle has resulted from eating grass where urea fertilizer was spread unevenly on pasture (Clarke 1975).

6.4 Other Land and Air Toxicity

Conc. (mg/L)	Species	Result	Reference
600	Frogs	LD _{LO} , subcutaneous	RTECS 1979
16 000	Pigeons	LD _{LO} , subcutaneous	RTECS 1979

6.5 Fate and Effect Studies

The effect of urea on blood constituents of the Indian catfish (*Meteropheustes fossils*) was studied; relatively high levels were required to produce an imbalance (Srivastava 1982).

In a trial of urea fertilization of an estuary for the purposes of increasing salmonid food items, it was found that the fertilization did not accelerate primary productivity or nitrogen regeneration. It was concluded that the fertilizer did not result in any appreciable enhancement of juvenile salmonid growth or survival (Stockner 1982).

Algal growth in rice fields was examined at 25 and 50 mg/L (as N) urea added to cultures of *Bracteacoccus minor*, *Scenedesmus* sp. and *Chlamydomonas* sp. Growth was accelerated by the addition but there was no significant difference between the 25 mg/L and 50 mg/L test groups (Barrett 1982).

Urea fertilizer was applied to a pasture and runoffs were measured. Maximum concentration of runoff was attained for ammonia nitrogen 3 weeks after application and for nitrate nitrogen 1 week after application. In the runoff, ammonia-nitrogen was only 0.3 percent of that applied, nitrogen nitrate was 1.0 percent, and total nitrogen was 7.1 percent of that applied. It was concluded that most applied urea will not run off (Sharpley 1983).

A forest fertilization study led to the conclusion that application rates less than 224 kg/ha (200 lb. N/acre) were ineffective in supplying nitrogen. Urea applications above this threshold brought about increases in soil nitrogen, pH, absorbed ammonia and cation exchange capacity, the latter especially in surface and litter material. Addition of urea appeared to have adverse effects on the uptake of phosphorus (Baker 1970).

6.6 Degradation

Degradation Rate	Species	Water Conditions	Reference
max. 11.6 mg/L/h,	psychrophilic	waste water treatment	Verschueren 1984
ave. 10.9 mg/L/h	bacteria	at 20°C	
max. 4.0 mg/L/h,	psychrophilic	waste water treatment	Verschueren 1984
ave. 3.2 mg/L/h	bacteria	at 2°C	

Conc. (mg/L)	Time (days)	Effect	Water Conditions	Reference
1 to 15	up to 14	degradation negligible	<8°C, river water	Evans 1973
1 to 15	4 to 6	degradation complete	20°C, river water	Evans 1973

6.7 Long-term Fate and Effects

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Urea will degrade to ammonia and eventually to nitrate. By providing a nitrogen source, it can enhance eutrophication (OHM-TADS 1981).

7 HUMAN HEALTH

There is little information in the published literature concerning the toxicological effects of test animal and human exposures to urea. Urea has been tested for mutagenicity and carcinogenicity. The NCI bioassay is reported as producing insufficient data to draw conclusions concerning the carcinogenic potential of urea (RTECS 1979). No data were found concerning the chemical's potential teratogenic effects. No toxicity reviews of urea were found in the literature. Urea has been reported in the EPA TSCA Inventory.

The toxicology data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. With the exception of data pertaining to mutagenicity and carcinogenicity, only acute (short-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

No recommended exposure limits for urea were found in the literature.

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
22 mg (3 d, intermit- tently)	Mild irritation.	RTECS 1979
SPECIES: Guinea Pig		
Unspecified	Treatment of guinea pigs with urea increased the effects of the subsequent sensitization with epoxy resins. Urea treatment increases the percentage of ani- mals sensitized by epoxy resins from 50 to 87 percent. Urea alone did not sensitize skin.	TDB (on-line) 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	When the urea concentration is higher in blood than in the eye, there is movement of water from eye to blood stream, reducing the volume of both the vitreous and aqueous humors and lowering intraocular pressure. When the concentration in the blood drops below that in the eye, water may move into the vitreous, pushing the lens forward and consequently increasing the risk of angle-closure glaucoma.	TDB (on-line) 1981
Unspecified	The eye is permeable to urea. A rebound elevation in intraocu- lar pressure and vitreous volume may occur after ocular hypoten- sive effect has terminated (about 8 to 12 hours after administration).	TDB (on-line) 1981
SPECIES: Rabbit		
0.2 mL of 10 M solution	When injected into the vitreous humor of rabbits, has caused inflammation.	TDB (on-line) 1981

- 7.3 Threshold Perception Properties
- 7.3.1 Odour.

Odour characteristics: Odourless or faint ammonia-like odour (CHRIS 1978).

7.3.2 Taste.

Parameter	Media	Concentration	Reference
Taste Recognition Threshold	in water	0.0501 moles/L (3 ppm)	ASTM 1980
Taste Detection in water Threshold		0.120 moles/L ASTM 1980 (7 ppm)	

Parameter Media		Concentration		Reference	
Taste Recognition in water Threshold		0.261 (16 p	moles/L pm)	ASTM 1980	
Taste Recognition Threshold	in water	0.316 (19 p	5 moles/L pm)	ASTM 1980	
Taste Recognition Threshold	in water	0.398 (24 p	8 moles/L pm)	ASTM 1980	
7.4 Toxicity	y Studies				
7.4.1 Inhalati	on. No da	ta.			
7.4.2 Ingestio	n.				
Exposure Level (and Duration)		Effects		Reference	
Acute Exposure					
SPECIES: Domesti	c Cattle				
511 mg/kg		LDLO		RTECS 1979	
SPECIES: Sheep					
2 g/kg		Lambs died in 90 to 200 minutes. TDB (Adult sheep exhibited almost continuous convulsions after 165 minutes. Sheep can consume up to 100 grams of urea a day, provided that the concentration of urea in ration does not exceed 6 percent. Liver dysfunction increases the sus- ceptibility to poisoning.		TDB (on-line) 1981	
SPECIES: Goat					
50 g Killed 4 out of 30 minutes.		Killed 4 out of 5 go 30 minutes.	oats within	TDB (on-line) 1981	
SPECIES: Ponies					
4 <i>5</i> 0 g		Killed 7 out of 8 po	onies.	TDB (on-line) 1981	

7.4.3 Subcutaneous.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Pig		
16 g/kg	LD _{LO}	RTECS 1979
SPECIES: Dog		
3000 mg/kg	LDLO	RTECS 1979
SPECIES: Rabbit		
3000 mg/kg	LD _{LO}	RTECS 1979

7.4.4 Mutagenicity and Carcinogenicity.

Exposure Level (and duration)	Effects	Reference
SPECIES: Hamster		
16 g/L (24 h)	Cytogenic analysis for chromo- somal aberrations in hamster fibroblast cells.	RTECS 1979
Unspecified	N.C.I. carcinogenesis assay has been completed. No report was made due to insufficient data.	RTECS 1979

7.5 Symptoms of Exposure

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

- 7.5.1 Inhalation. No data.
- 7.5.2 Ingestion. No data.
- 7.5.3 Skin.
- 1. Mild irritation (RTECS 1979).

7.5.4 Eyes.

1. Irritation (CHRIS 1978).

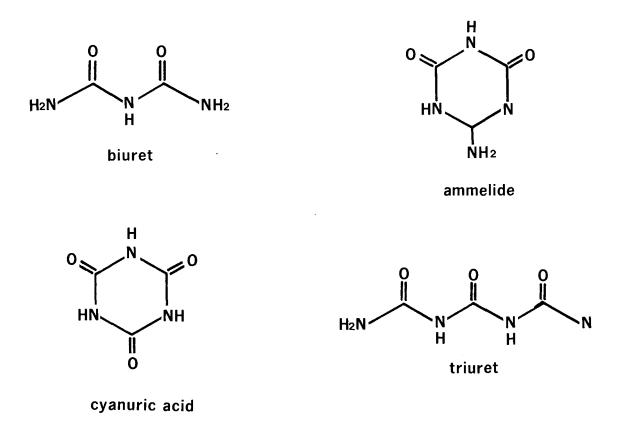
2. Changes in intraocular pressure (TDB (on-line) 1981).

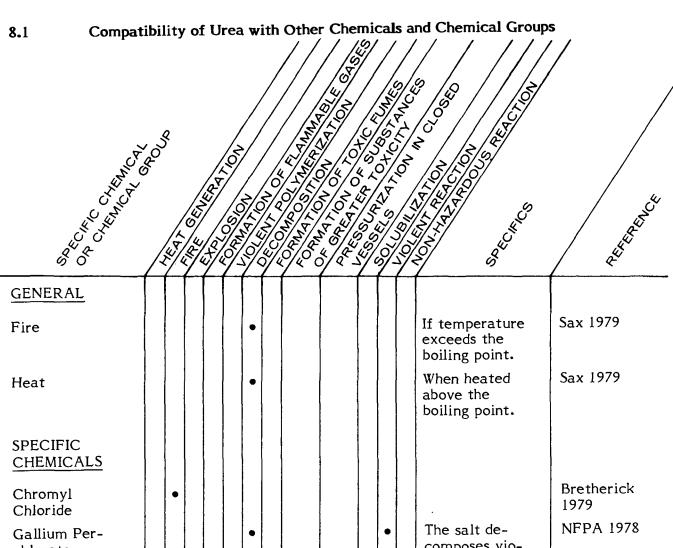
7.6 Human Toxicity to Decay or Combustion Products

Urea decomposes at atmospheric pressure and at its melting point to ammonia, biuret, cyanuric acid, ammelide and triuret (Kirk-Othmer 1983).

Ammonia is a colourless gas with a penetrating, pungent and suffocating odour. It is detectable by odour at concentrations as low as 5 ppm. At 100 ppm, irritation of mucous membranes becomes noticeable; prolonged exposure to concentrations above 400 ppm may destroy mucous surfaces by dissolving or emulsifying keratin, fat, and cholesterol. The most frequent cause of death from exposure to ammonia is pulmonary edema. Its TLV® is 25 ppm (8 h - TWA) and the STEL is 35 ppm (TLV 1983).

Little information is available on the toxicity of biuret, cyanuric acid, ammelide and triuret (all shown below).





composes viochlorate lently on heating. Nitrosyl Per-• chlorate Sodium Nitrite The liquid he-Titanium Tetraxaurea complex chloride formed decomposes violently at above 90°С.

Bretherick

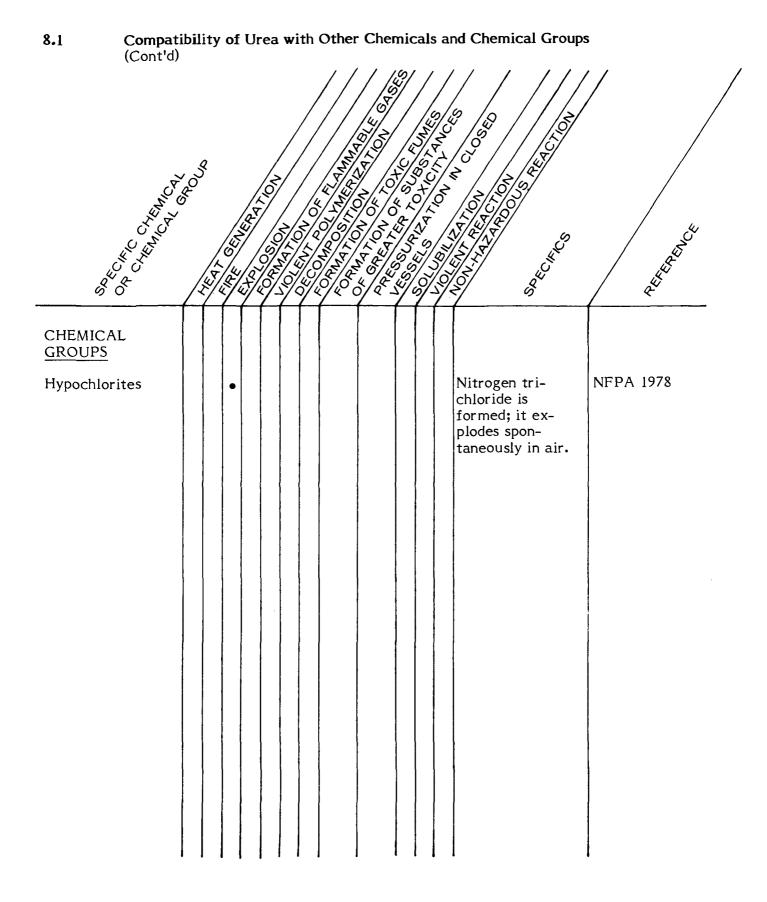
Bretherick

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1979

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1979



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. Urea is a nonflammable solid; it may become slightly dangerous when heated to its decomposition temperature (133°C) (Sherritt MSDS 1980).

9.1.2 Fire Extinguishing Agents. Most fire extinguishing agents may be used in fires involving urea.

9.1.3 Spill Actions, Cleanup and Treatment.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Avoid skin contact (Olin MSDS 1981).

9.1.3.2 Spills on land. For spills of solid urea, shovel contaminated material into containers for disposal (Olin MSDS 1981). For spills of urea in solution form, contain if possible by forming mechanical and/or chemical barriers to prevent spreading. Neutralize with vinegar or dilute acid (EPA 670/2-75-042).

9.1.3.3 Spills in water. Contain if possible. Apply activated carbon at 10 percent the spill amount over the region occupied by 10 mg/L or greater concentrations. Use mechanical dredge or lifts to remove the immobilized masses of pollutants (EPA 670/2-75-042).

The following sorbent materials may be used in spill situations: Amberlite XAD resins, Dowex 50WX8, and Amberlite IRA 900 (CG-D-38-76).

9.1.4 Treatment and Disposal. Production plants may have a number of treatment processes in place; recovered urea-contaminated water may be passed to them (Bruls 1982). Urea also degrades in standard sewage plants at temperatures around 20°C so this option may also be used.

Reverse osmosis has been tested on urea solutions. Cellulose acetate membranes removed 20-40 percent of urea in a single pass, cross-linked polyethylenimine removed 70-80 percent, and aromatic polyamide membranes removed 30 to 50 percent (Fang 1976).

In the event that the collected material is not contaminated with hazardous chemicals, the urea can be spread as a fertilizer; rates of 200-400 kg/ha are recommended.

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

If the spilled material is known to be urea:

- Safety goggles, coveralls, impervious gloves and boots should be worn (Olin MSDS 1981).
- If intense heat prevails, a cannister (organic and acid gas) mask should be worn (OHM-TADS 1981).

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information. 59

11 ANALYTICAL METHODS

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

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

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought. If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Detection of Urea in Air

Since urea is nonvolatile and is generally shipped in pellet form, contamination of the air would not be expected in the event of a spill.

11.2 Quantitative Method for the Detection of Urea in Water

11.2.1 Microcoulometry (ASTM 1979). Urea in water may be determined as total nitrogen in concentrations from 0.5 to 100 mg/L.

A minimum volume of 2 L of representative sample is collected in an appropriate container. A 3 μ L aliquot of sample is injected into a stream of hydrogen gas flowing at 300 mL/min through a quartz pyrolysis tube. The pyrolysis tube contains granular 10/40 mesh nickel and is housed in a pyrolysis furnace with three separate heat zones, capable of reaching the following temperatures: inlet zone, 700°C; pyrolysis zone, 800°C; and outlet zone, 800°C. The pyrolysis tube should also have 50 percent sodium hydroxide on asbestos at the outlet to serve as an acid gas scrubber. The titration cell contains a sensor-reference pair of electrodes and a stirrer set to produce a slight vortex. The microcoulometer has variable attenuation and bias voltage set at 110 mV with a gain of 400 to 600.

The sample concentration is determined by a suitable electronic integrator in conjuction with a calibration curve.

11.3 Qualitative Method for the Detection of Urea in Water

The sample is collected as in Section 11.2.1. Urea may be determined qualitatively by reaction with nitrous acid. A suitable volume of sample is placed in a test tube and nitrous acid is added. The evolution of carbon dioxide indicates the presence of urea (Morrison 1976).

11.4 Quantitative Method for the Detection of Urea in Soil

11.4.1 Spectrophotometric (Mulvaney 1979). Concentrations up to 100 μ g/mL of urea in soil may be determined by spectrophotometric measurement.

A soil sample is extracted with 2 M potassium chloride-phenyl-mercuric acetate solution. A 10 mL volume of extract is transferred to a 50 mL volumetric flask and diluted with 10 mL of 2 M potassium chloride-phenylmercuric acetate. A 30 mL volume of colour reagent is added to the mixture. The reagent is prepared by mixing 50 mL of diacetyl monoxime (2.5 g/100 mL) and 30 mL of thiosemicarbazide (0.25 g/100 mL) and diluting to 1 L with acid reagent. The acid reagent is prepared by mixing 40 mL of concentrated sulphuric acid and 1 L of 85 percent w/w phosphoric acid and diluting to 2 L with distilled water. The colour reagent must be prepared immediately before use.

The sample treatment continues as follows. After the addition of the colour reagent, the mixture is swirled and placed in a water bath for 30 minutes at 85°C. The sample is then water-cooled and made up to 50 mL if sample loss has occurred. The sample absorbance is determined at 527 nm using a suitable spectrophotometer. The sample concentration is determined using a calibration curve.

11.5 Qualitative Method for the Detection of Urea in Soil

The sample is collected as in Section 11.4.1. Urea may be determined qualitatively by reaction with nitrous acid. A suitable volume of sample is placed in a test tube and nitrous acid is added. The evolution of carbon dioxide indicates the presence of urea (Morrison 1976).

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EnviroTIPS

Common Abbreviations

BOD b.p.		biological oxygen demand boiling point	MMAD	mass median aerodynamic 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
	2	Law New With a With	NIOSH	National Institute for
g		gram hectare	NIOSII	Occupational Safety and
ha				Health
Hg IDLH		mercury		riealti
IDLI		immediately dangerous to life and health	-	nonomotro
Imp. col			nm	nanometre
Imp. gal.		imperial gallon	0	ortho
in.		inch	OC	open cup
J		joule	p P _C	para
kg		kilogram	PC	critical pressure
kJ		kilojoule	PËL	permissible exposure level
km		kilometre	рН	measure of acidity/
kPa		kilopascal	Test.	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
LD50		lethal dose fifty	STEL	short-term exposure limit
LDLO		lethal dose low	STIL	short-term inhalation limit
LEL		lower explosive limit	Τ _C	critical temperature
LFL		lower flammability limit	TCLO	toxic concentration low
m		metre	Td	decomposition temperature
m		meta	TDLO	toxic dose low
Μ		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
				995 - 1921 - 1988 1995 - 1921 - 1988

μg	microgram		
μm	micrometre		
°Be	degrees Baumé (density)		

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