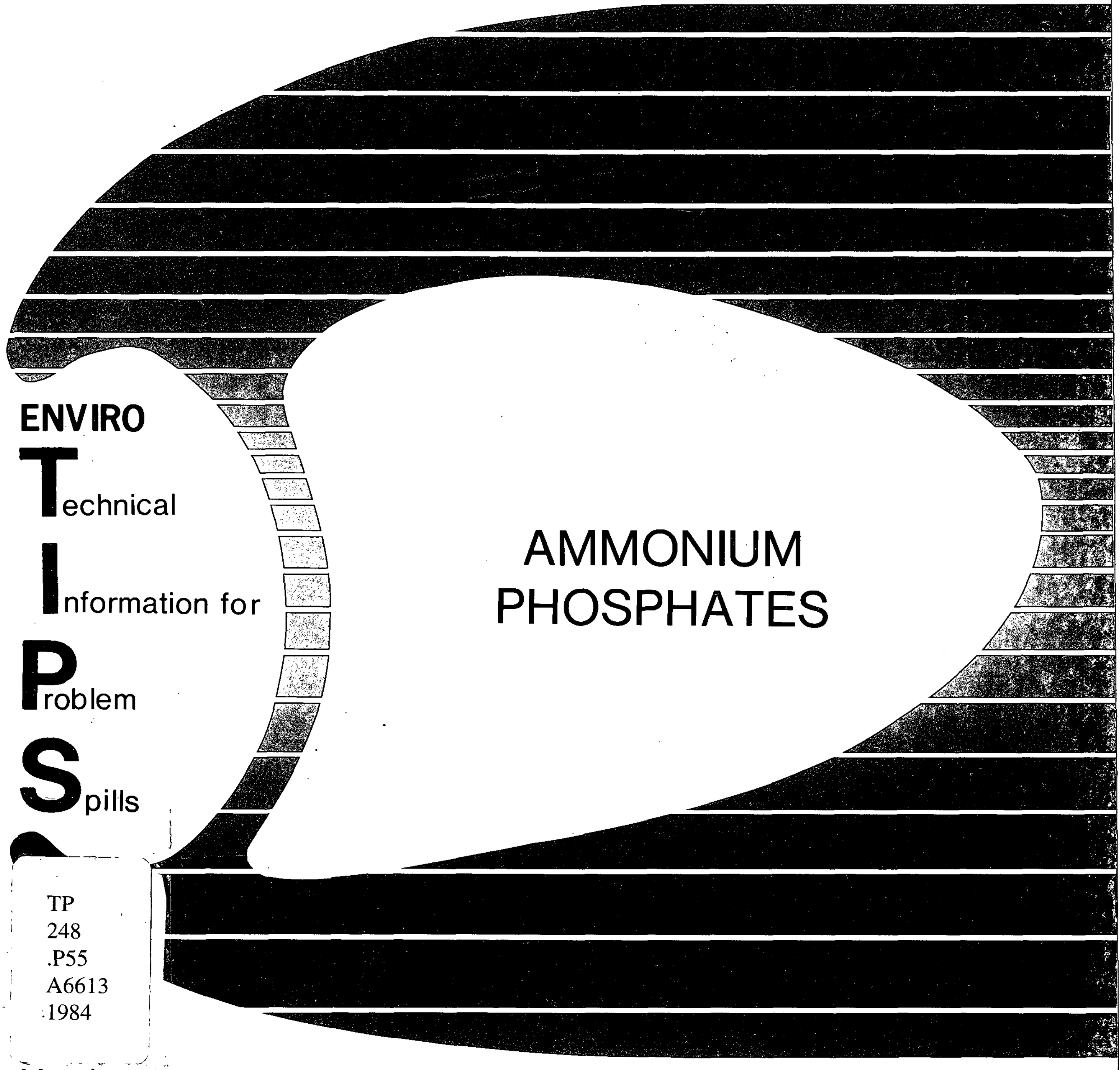
Environment Canada
Environmental Protection Service

Environnement Canada
Service de la protection de l'environnement



ENVIRO

Technical
Information for
Problem
Spills

AMMONIUM PHOSPHATES

March 1984

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

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

AMMONIUM PHOSPHATES

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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

March 1984

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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 rewrote the text, drafted illustrations and incorporated all comments and additions.

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

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1 SUMMARY

AMMONIUM PHOSPHATES ($NH_4H_2PO_4$ and $(NH_4)_2HPO_4$)

White granular or powdered solids, odourless or only faint odours

SYNONYMS

$(NH_4)_2HPO_4$; D.A.P.; Diammonium Phosphate; Ammonium Phosphate, dibasic; Ammonium Phosphate, secondary; Diammonium Orthophosphate; Diammonium Hydrogen Phosphate

$(NH_4)H_2PO_4$; M.A.P.; Monoammonium Phosphate; Monoammonium Orthophosphate; Ammonium Phosphate, primary; Ammonium Acid Phosphate; Ammonium Biphosphate; Ammonium Dihydrogen Phosphate

IDENTIFICATION NUMBERS

UN. No. Not required; STCC No. 4918704; CAS No. (D.A.P.) 7783-28-0, (M.A.P.) 7722-76-1; OHM-TADS No. 7216590

GRADES & PURITIES

D.A.P.	- technical:	53 percent P_2O_5 and 25 percent NH_3
	- food:	53.5 percent P_2O_5 and 25.4 percent NH_3
M.A.P.	- technical:	60 percent P_2O_5 and 14.5 percent NH_3
	- feed:	>24 percent phosphorus
	- food:	61.5 percent P_2O_5 and 14.5 percent NH_3

Fertilizer Grade:	18-46-0 (22 percent NH_3)
	11-48-0 (13 percent NH_3)
	11-51-0 (13 percent NH_3)

IMMEDIATE CONCERNS

Fire: Not combustible. Toxic and irritating fumes of ammonia, phosphorus oxides and nitrogen oxides may form in fires

Human Health: Low order of toxicity by inhalation, contact or ingestion

Environment: Harmful to aquatic life in high concentrations

PHYSICAL PROPERTY DATA

	D.A.P.	M.A.P.
State (15°C, 1 atm):	solid	solid
Melting Point:	decomposes at 155°C	190°C
Flammability:	not flammable	not flammable
Specific Gravity (water=1):	1.619 (20°C)	1.803 (19°C)
Solubility (in water):	69 g/100 g (20°C)	38 g/100 g (20°C)
Behaviour (in water):	sinks and mixes	sinks and mixes
Odour Threshold:	odourless	odourless

ENVIRONMENTAL CONCERNS

Ammonium phosphates are nutrients in waters. Spills of ammonium phosphates can stimulate algal blooms and may alter species population balances in the aquatic environment. There is no potential for bioaccumulation or food chain contamination.

HUMAN HEALTH

No TLV or IDLH established

Exposure Effects

Inhalation: Monobasic form: Dust is irritating to eyes, nose and throat. If inhaled, causes coughing or difficult breathing

Dibasic form: Ammonia vapours released as a result of decomposition in closed areas can cause coughing, difficult breathing and lung irritation

Contact: Contact with solid forms may cause mild irritation to skin and eyes

IMMEDIATE ACTION

Spill Control

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

Fire Control

Not combustible.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill. Shovel into containers with covers

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

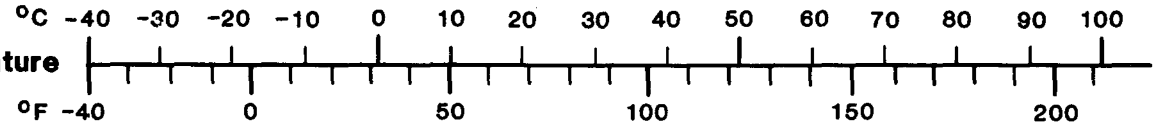
2 PHYSICAL AND CHEMICAL DATA

Physical State Properties	Monoammonium Phosphate	Diammonium Phosphate
Appearance	Pure: White, anhydrous crystalline salt (ERCO PDS 1981a) Fertilizer Grade: Greenish granules - if made from western rock Grey granules - if made from Florida rock (CCPA 1982)	Pure: White, anhydrous crystalline salt (ERCO PDS 1981b) Fertilizer Grade: Greenish granules - if made from western rock Grey to brown granules - if made from Florida rock (CCPA 1982)
Usual shipping state(s)	Crystalline salt (ERCO PDS 1981a)	Crystalline salt (ERCO PDS 1981b)
Physical state at 15°C, 1 atm	Solid	Solid
Melting point	190°C (CRC 1980)	Decomposes at 155°C before melting (CRC 1980)
Decomposition temperature		155°C (CRC 1980)
Densities		
Bulk density	990 kg/m^3 (ERCO PDS 1981a)	990 kg/m^3 (ERCO PDS 1981b)
Specific gravity	1.803 (19°C) (CRC 1980)	1.619 (20°C) (CRC 1980)
Fire Properties		
Flammability	Nonflammable (ERCO PDS 1981a)	Nonflammable (ERCO PDS 1981b)
Decomposition products	Ammonia and phosphoric acids	
Behaviour in a fire	May liberate ammonia, oxides of nitrogen, and phosphorus (U.S. DOL MSDS 1979)	
Other Properties		
Molecular weight of pure substance	115.03 (CRC 1980)	132.05 (CRC 1980)
Constituent components of typical food grade	61.5% P_2O_5 14.5% NH_3 0.25% moisture (ERCO PDS 1981a)	53.5% P_2O_5 25.4% NH_3 0.3% moisture (ERCO PDS 1981b)

	Monoammonium Phosphate	Diammonium Phosphate
Refractive index	1.479 (CRC 1980)	1.52 (CRC 1980)
Heat of formation	-1445 kJ/mole (25°C) (Lange's Handbook 1979)	-1567 kJ/mole (25°C) (Lange's Handbook 1979)
Heat capacity		
constant pressure (Cp)	142 J/mole•°C (25°C) (Lange's Handbook 1979)	188 J/mole•°C (25°C) (Lange's Handbook 1979)
pH of aqueous solution	4.5 (1% sol'n) (20°C) (ERCO PDS 1981a)	8.0 (1% sol'n) (20°C) (ERCO PDS 1981b)
Solubility		
In water	22 g/100 g (0°C) 38 g/100 g (20°C) 168 g/100 g (100°C) (ERCO PDS 1981a)	43 g/100 g (0°C) 69 g/100 g (20°C) 97 g/100 g (60°C) (ERCO PDS 1981b)
In other common materials	*Insoluble in acetone* (CRC 1980)	*Insoluble in ethanol, acetone and ammonia* (CRC 1980)

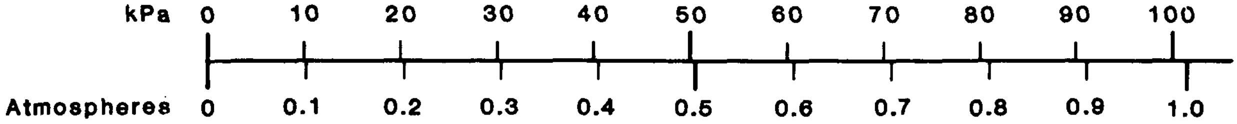
CONVERSION NOMOGRAMS

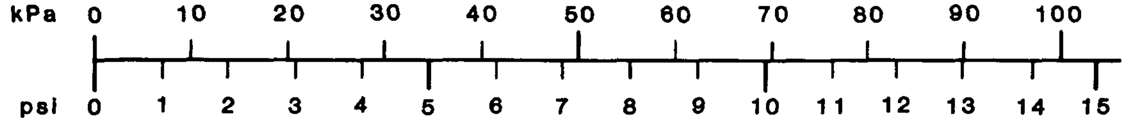
Temperature

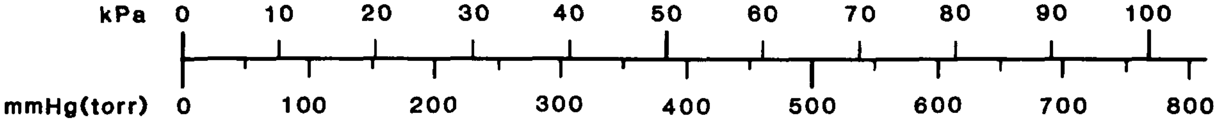


Pressure

1 kPa = 1,000 Pa







Viscosity

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

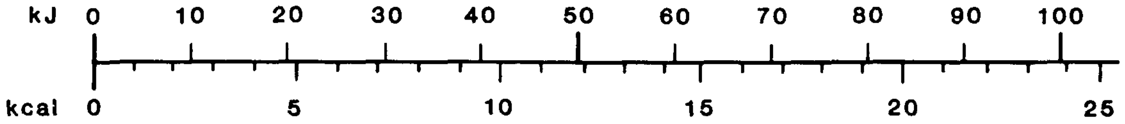
Kinematic 1 m^2/s = 1,000,000 centistokes (cSt)

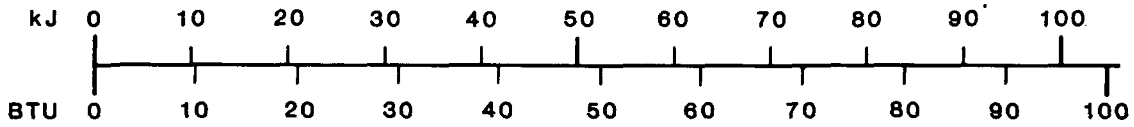
Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat)

1 kJ = 1,000 J





Density

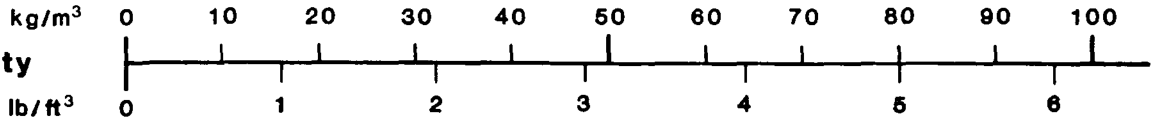
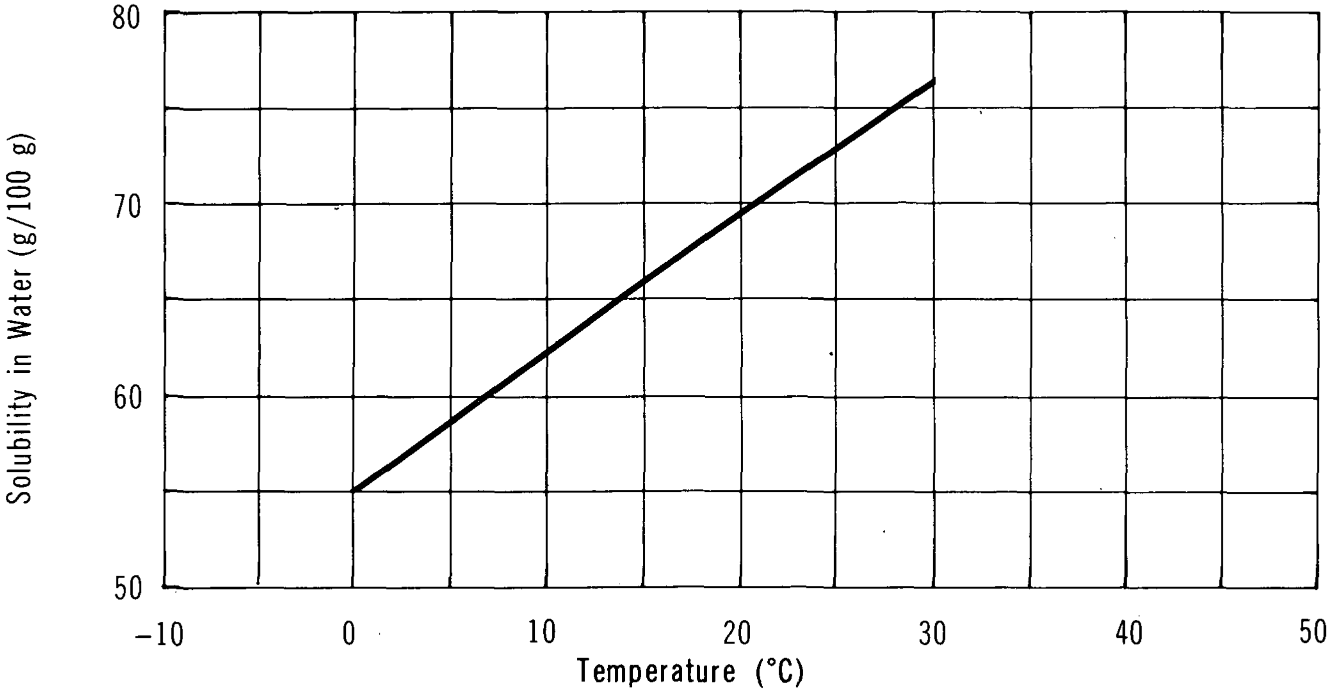


FIGURE 1

DIAMMONIUM PHOSPHATE **SOLUBILITY IN WATER vs TEMPERATURE**

Reference: CHRIS 1978



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities

3.1.1 Diammonium Phosphate. Diammonium phosphate is an anhydrous, white/grey to brown granular material and is shipped most commonly in fertilizer grades. The technical grade is available in granular and 100-mesh powdered free-flowing forms, with a minimum of 53.0 percent P_2O_5 and 25.0 percent NH_3 (Stauffer IDS 1981). The food grade is in a crystalline form, with a minimum of 53.5 percent P_2O_5 and 25.4 percent NH_3 (ERCO PDS 1981b).

3.1.2 Monoammonium Phosphate. Monoammonium phosphate is a white granular or powdered solid and is available in a technical, fertilizer, food or feed grade (Stauffer IDS 1981; IMC 1976; ERCO PDS 1981a). The technical grade is in granular or powdered free-flowing forms, with a minimum of 60 percent P_2O_5 and a minimum of 14.5 percent NH_3 (Stauffer IDS 1981). The feed grade is in free-flowing granular form, with a minimum of 24 percent phosphorus (IMC 1976). The food grade is in crystalline form, with a minimum of 61.5 percent P_2O_5 and 14.5 percent NH_3 (ERCO PDS 1981a).

3.2 Domestic Manufacturers (CBG 1980; CCPA 1981; Scott 1979)

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

Belledune Fertilizer, Division of
Canada Wire and Cable
147 Laird Drive
Toronto, Ontario
M4G 3W1
(416) 421-0440

C-I-L Inc.
45 Sheppard Avenue East
Willowdale, Ontario
M2N 2Z9
(416) 226-6110

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

Erco Industries Ltd.
2 Gibbs Road
Islington, Ontario
M9B 1R1
(416) 239-7111

Esso Chemical Canada
2300 Yonge Street
Toronto, Ontario
M5W 1L3
(416) 488-6600

International Minerals & Chemical
Corp. (Canada) Ltd. (IMC)
P.O. Box 310
Esterhazy, Saskatchewan
S0A 0X0
(306) 745-3931

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

Western Co-operative Fertilizers
11111 Barlow Trail S.E.
P.O. Box 2500
Calgary, Alberta
T2P 2X1
(403) 279-4421

3.3 Other Suppliers (Corpus 1981)

All suppliers listed distribute the product as fertilizer.

Agricultural Chemicals
Highway 22
London, Ontario
(519) 471-6550

Cyanamid Canada Inc.
19400 TransCanada Highway
Baie D'Urfe, Quebec
H9X 3N7
(514) 457-2110

Cooperative Federee du Quebec
1055 Marche Central
Montreal, Quebec
H4N 1K3
(514) 384-6450

United Co-Operatives of Ontario
151 City Centre Drive
Mississauga, Ontario
L5B 1M7
(416) 270-3560

3.4 Major Transportation Routes

Current Canadian production of ammonium phosphates is very widespread, occurring in 6 out of 10 provinces. The largest production facilities are near Fort Saskatchewan and near Calgary, Alberta; in central New Brunswick; and in Kimberley and Trail, B.C.

3.5 Production Levels (Corpus 1982; PC 1981)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1981)
Belledune Fertilizer, Belledune, N.B.	272
C-I-L Inc., Courtright, Ont.	170
Cominco, Trail, B.C.	160
Cominco, Kimberley, B.C.	175
Erco Industries, Buckingham, Que.	5
Esso Chemical Canada, Redwater, Alta.*	430
Sherritt Gordon Mines, Ft. Saskatchewan, Alta.	123
Simplot Chemical, Brandon, Man.	145
Western Cooperative Fertilizers, Calgary, Alta.	260
Western Cooperative Fertilizers, Medicine Hat, Alta.	181
TOTAL	1,921

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1981)
Domestic Production (1981)	1,428.0
Imports (1981)	259.5
TOTAL SUPPLY	1,687.5

*Includes phosphate for nitrate-phosphate blend.

3.6 Manufacture of Ammonium Phosphates

3.6.1 General. Phosphoric acid is neutralized with ammonia to form monoammonium and diammonium phosphates.

3.6.2 Raw Materials. The raw materials used are ammonia and acid-process phosphoric acid.

3.6.3 Process. The following process applies for the production of general fertilizers only. Ammonia gas and 30 to 47 percent phosphoric acid are mixed in either a mixing tank or a continuous flow reactor. The reaction produces a slurry of monoammonium or diammonium phosphate. Overall reactions are:

$$NH_3 + H_3PO_4 \rightarrow (NH_4)\,H_2PO_4$$

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2\,HPO_4$$

depending on the proportion of ammonia used. The heat of reaction evaporates part of the water in the acid charge. From the reactor, the slurry is fed to a mill or drum where fines from previous batches are added; this promotes granule growth. The slurry is then discharged to a rotary dryer, then cooled and screened. Coarse product is ground, combined with fines and recycled to promote granule growth (Sherritt).

3.7 Future Development (Corpus 1982)

Esso Chemical Canada will be expanding its Redwater plant in Alberta for an increase in its ammonium phosphates capacity in the near future. Sherritt Gordon Mines are planning some expansion at their Fort Saskatchewan plant in Alberta.

3.8 Major Uses in Canada

3.8.1 Monoammonium Phosphate. It is used for specialty fertilizers, food ingredients, paints, an agent in dye baths, powder fire extinguishers and flameproofing of fabrics, wood and papers (ERCO PDS 1981a).

3.8.2 Diammonium Phosphate. It is used in fertilizers, food ingredients, flame retardants and pharmaceuticals (ERCO PDS 1981b).

3.9 Major Buyers in Canada (Corpus 1981; CBG 1980)

Agricultural Chemicals, London, Ontario
A & K Petro-Chem, Weston, Ont.
Alberta Wheat Pool, Edmonton, Alta.
Canada Colours, Toronto, Ont.
Cargill Grain, Winnipeg, Man.
Cooperative Federee du Quebec, Montreal, Que.
Cyanamid Canada, Montreal, Que.
Harrisons & Crosfield, Toronto, Ont.
Kingsley & Keith, Toronto, Ont.
Nitrochem, Maitland, Ont.
Mallinckrodt, Pt. Claire, Que.
Manitoba Pool Elevators, Winnipeg, Man.
Monsanto, Mississauga, Ont.
Noranda, Toronto, Ont.
Saskatchewan Wheat Pool, Regina, Sask.
Swift Canadian, Toronto, Ont.
United Co-operatives of Ontario, Mississauga, Ont.
United Grain Growers, Regina, Sask.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation

4.1.1 Bulk Shipment. Railway tankers and highway tank trucks are the basic means of transport for ammonium phosphates. The monobasic and dibasic forms are shipped as solids and sometimes in solution form.

4.1.1.1 Railway cars. As a solid granular material, ammonium phosphates are shipped in bagged form on box cars; as a solution, they are shipped in nonregulated tankers, with DOT/CTC 111A60W5 and 111A60W1 rail cars being most common (TCM 1979). These cars are described in Table 2 (TCM 1979).

Figure 2 shows a DOT/CTC 111A60W1 railway car used to transport ammonium phosphates solutions; Table 3 indicates details associated with this drawing (TCM 1979). As indicated in Table 2, tankers transporting ammonium phosphates solutions may be unloaded from top or bottom, depending on the class of car selected.

4.1.1.2 Motor vehicles. Trucks are used to carry shipments of ammonium phosphates in solid form. Flat beds or enclosed transport trucks carry bagged material while dump trucks or pneumatic-type trucks are used for bulk shipment (PC 1982). Liquid ammonium phosphates in solution form may be transported in nonregulated cargo tankers (PC 1982).

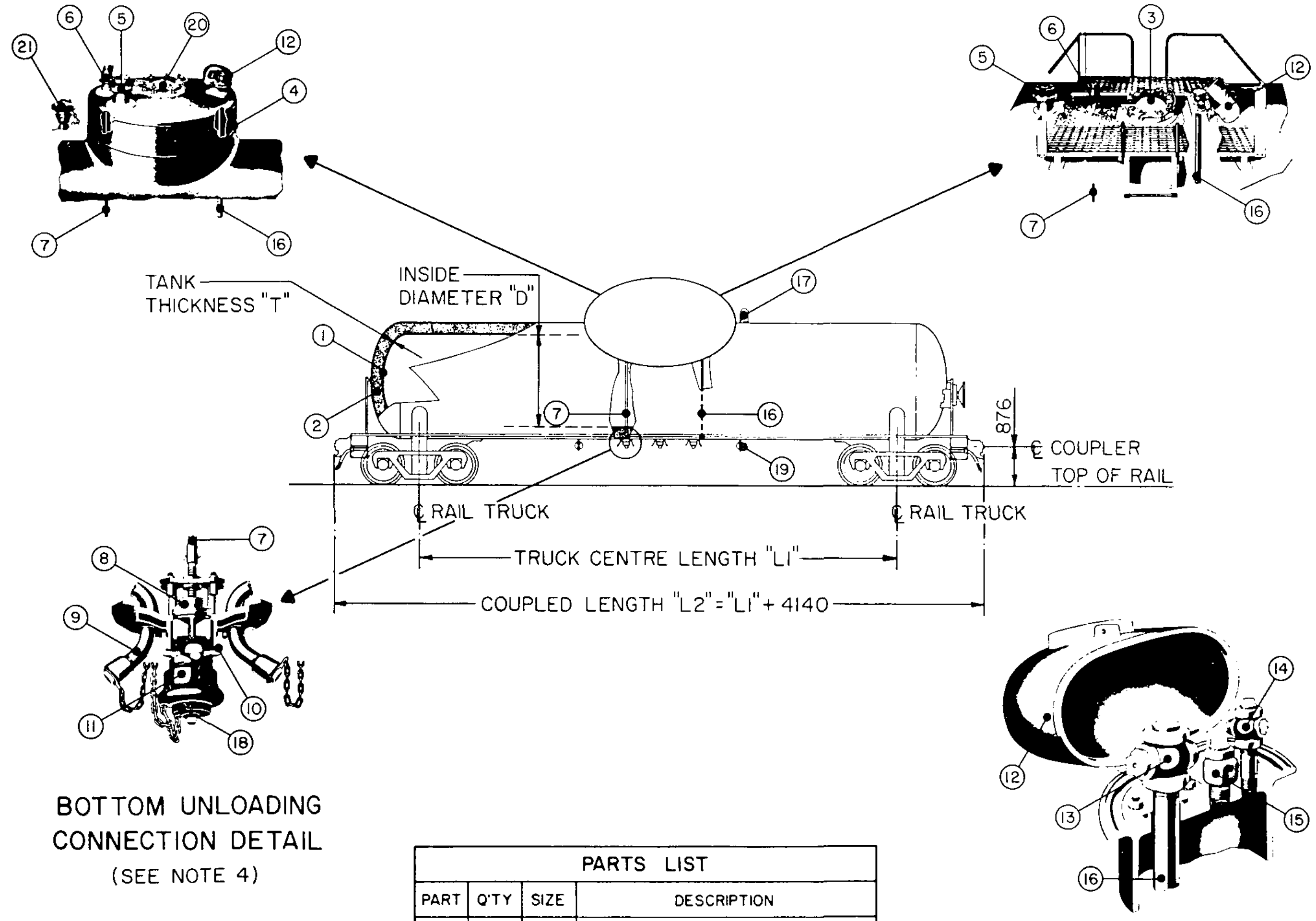
TABLE 2 RAILWAY TANK CAR DESCRIPTIONS

DOT/CTC* Specification Numbers	Description
111A60W5	Steel fusion-welded tank without dome. Uninsulated or insulated. Rubber-lined tank. 2% minimum outage. Gauging device. Top unloading arrangement required. Safety vent set at 414 kPa (60 psi). Bottom outlet or washout prohibited.
111A60W1	Same as 111A60W5 except no rubber lining and top unloading is not mandatory.
111A60W1 (1L)	Same as 111A60W1 except it is interior coated.

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

FIGURE 2

RAILWAY TANK CAR



BOTTOM UNLOADING CONNECTION DETAIL
(SEE NOTE 4)

TOP UNLOADING CONNECTION DETAIL

PARTS LIST

PART	Q'TY	SIZE	DESCRIPTION
1	1	-	TANK SHELL
*2	-	-	INSULATION
*3	1	-	DOMELESS MANWAY COVER
*4	1	-	DOME
5	1	-	SAFETY VALVE
*6	1 to 3	-	STUFFING BOX
*7	1 to 3	-	OPERATING ROD
*8	1 to 3	150	INTERNAL STOP VALVE
*9	1 to 3	25	STEAM JACKET CONNECTION
*10	1 to 3	150	OUTLET NOZZLE EXTENSION
*11	1 to 3	-	CAP
*12	1	-	PROTECTIVE HOUSING COVER
*13	1	50	TOP UNLOADING CONNECTION VALVE
*14	1	25	AIR CONNECTION VALVE
*15	1	-	VACUUM RELIEF VALVE
*16	1	50	EDUCTION PIPE
*17	1	-	GAUGING DEVICE
*18	1 to 3	50	PIPE PLUG
*19	2	25	STEAM COIL CONNECTION VALVE
*20	1	-	DOME MANWAY COVER
*21	1	50	SAFETY VENT ASSEMBLY

NOTES:

1 - ALL DIMENSIONS IN MILLIMETRES.

2 - THIS DRAWING TO BE USED IN CONJUNCTION WITH RAILWAY CAR TABLE II IN TEXT. MATERIALS, CAPACITY, WEIGHTS AND LETTERED DIMENSIONS SPECIFIED THEREIN.

3 - BOTTOM UNLOADING CONNECTIONS VARY IN NUMBER FROM ONE TO THREE DEPENDING ON MATERIAL TRANSPORTED. SEE TABLE II.

4 - END OPTIONS FOR BOTTOM UNLOADING INCLUDE SLUICE VALVE, BOLTED BLANK FLANGE, SCREW CAP. SEE TABLE II.

5 - "*" INDICATES THAT PART MAY OR MAY NOT BE REQUIRED. SEE TABLE II.

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

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

4.1.2 Packaging. In addition to bulk shipments, ammonium phosphates are shipped in paper bags. The granular material is packaged in 20, 40 or 45 kg net weight paper bags; the powdered form, usually 100 mesh, is packaged in 20, 23, or 40 kg net weight paper bags (Stauffer MSDS 1981).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures. Both rail cars and highway tankers used to transport solid ammonium phosphates materials are unloaded in the same manner. Normal solids handling equipment such as front end loaders, conveyors, bins, etc., are used (PC 1982).

Solutions of ammonium phosphates are off-loaded from the top of rail cars or trucks by pump or from the bottom by pump or gravity flow. During top off-loading, the 51 mm (2 in.) pump suction line or unloading line is connected to the discharge valve at the top of the car; during bottom unloading, this line is attached to one of the 152 mm (6 in.) bottom outlets, complete with reducer, and then the internal bottom valve is opened by turning the handle at the top of the tanker. This bottom outlet may also be discharged to a storage tank by gravity alone (PC 1982).

4.2.2 Specifications and Materials. Dry ammonium phosphates, both monobasic and dibasic, are handled by materials commonly used in the construction of process equipment and storage facilities. For aqueous solutions, stainless steel material is recommended (Stauffer MSDS 1981).

Schedule 40 piping, flanged at joints, should be used. Fittings should be cast stainless steel. Installations of flexible line may be constructed of standard fittings using a number of elbows or natural rubber hosing. The flexible bellow-type expansion joints may also be used for flexible sections of the unloading line (Dow PPS 1972). For valving, cast iron or cast steel diaphragm valves lined with chlorinated polyether or polyvinylidene chloride resin serve adequately (Dow PPS 1972).

Centrifugal pumps with wet end parts of 304 or 316 stainless steel are recommended (HIS 1969).

4.3 Compatibility with Materials of Construction

The compatibility of ammonium phosphates with materials of construction is indicated in Table 4. The unbracketed abbreviations are derived from Table 5. 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 4 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical Conc.	Chemical Temp. (°C)	Material of Construction Recommended	Material of Construction Conditional	Material of Construction Not Recommended
1. Pipes and Fittings		60	PVC I PVC II (DPPED 1967)		
		66	PVDC (DCRG 1978)		
		79	PP (DCRG 1978)		
		121	Chlorinated Polyether (DCRG 1978)		
		135	PVDF (DCRG 1978)		
		To operating limit of material	PVC I ABS PE (MWPP 1978)		
2. Valves	All	Boiling	SS 316 SSJ-20 (JSSV 1979)		
3. Pumps	(Dibasic, Mono-basic) 65%	66	GRP with FPM "O" Ring		
	(Dibasic) Aqueous Solution		All Iron SS 304 SS 316 Monel (HIS 1969)		

TABLE 4 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
4. Others	5%	20	SS 302 SS 304 SS 316 SS 430 (ASS)	SS 410 (ASS)	
	Saturated	20	SS 302 SS 304 SS 316 SS 430		
	All	60	uPVC PE PP POM NR* NBR IIR EPDM CR FPM CSM (GF)		
		60	PVC (TPS 1978)		
		82	PP (TPS 1978)		
		85	CPVC (TPS 1978)		
			SBR CR NBR IIR CSM EPDM (GPP)	NR (GPP)	
	10% to solid	24 to 100	Glass (CDS 1967)		
	20, 30%	24	Glass (CDS 1967)		
	solid	24	Concrete (CDS 1967)		

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

TABLE 5 MATERIALS OF CONSTRUCTION

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

5 CONTAMINANT TRANSPORT

5.1 General Summary

Ammonium phosphates are transported as solids, in granular form, or as aqueous solutions. When spilled in water, all forms will dissolve rapidly. When spilled on soil, the aqueous solutions will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Movement of ammonium phosphates toward the water table may be an environmental concern.

Because ammonium phosphates are nonvolatile, dispersion in air is not a problem.

Factors considered regarding the movement of ammonium phosphates spills in water and soil are:

- Contaminant Transport
  - Leak or spill
    - Rate of discharge
    - Percent remaining
  - Water
    - Diffusion rate
  - Soil
    - Depth and time of penetration

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. Ammonium phosphates are transported as solid granular materials or as aqueous solutions. In aqueous form, ammonium phosphates are commonly transported in cylindrical 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.

If a tank car loaded with aqueous solution 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 low volatility of ammonium phosphates solutions 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.

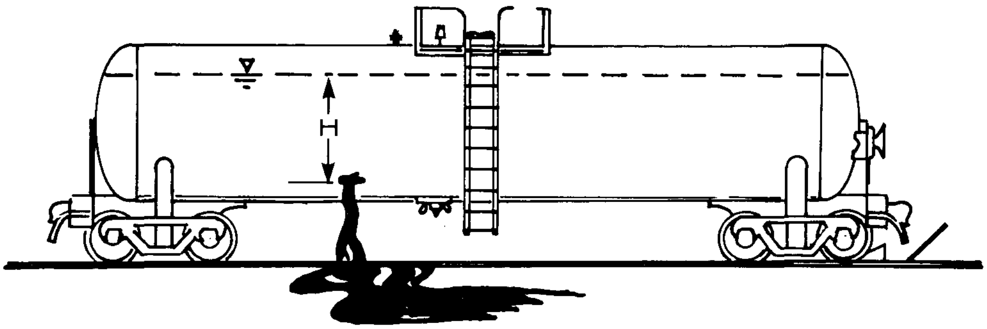


FIGURE 3 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

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 the hole size (A) and shape, the height of the fluid above the puncture hole (H) and a coefficient of discharge (Cd). 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 4: Percent remaining versus time. Figure 4 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car (2.75 m ∅ x 13.4 m long) is assumed to be initially full (at t=0) with a volume of about 80,000 L of ammonium phosphates solution. 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 5: Discharge rate versus time. Figure 5 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.

FIGURE 4

AMMONIUM PHOSPHATES

PERCENT REMAINING VS TIME

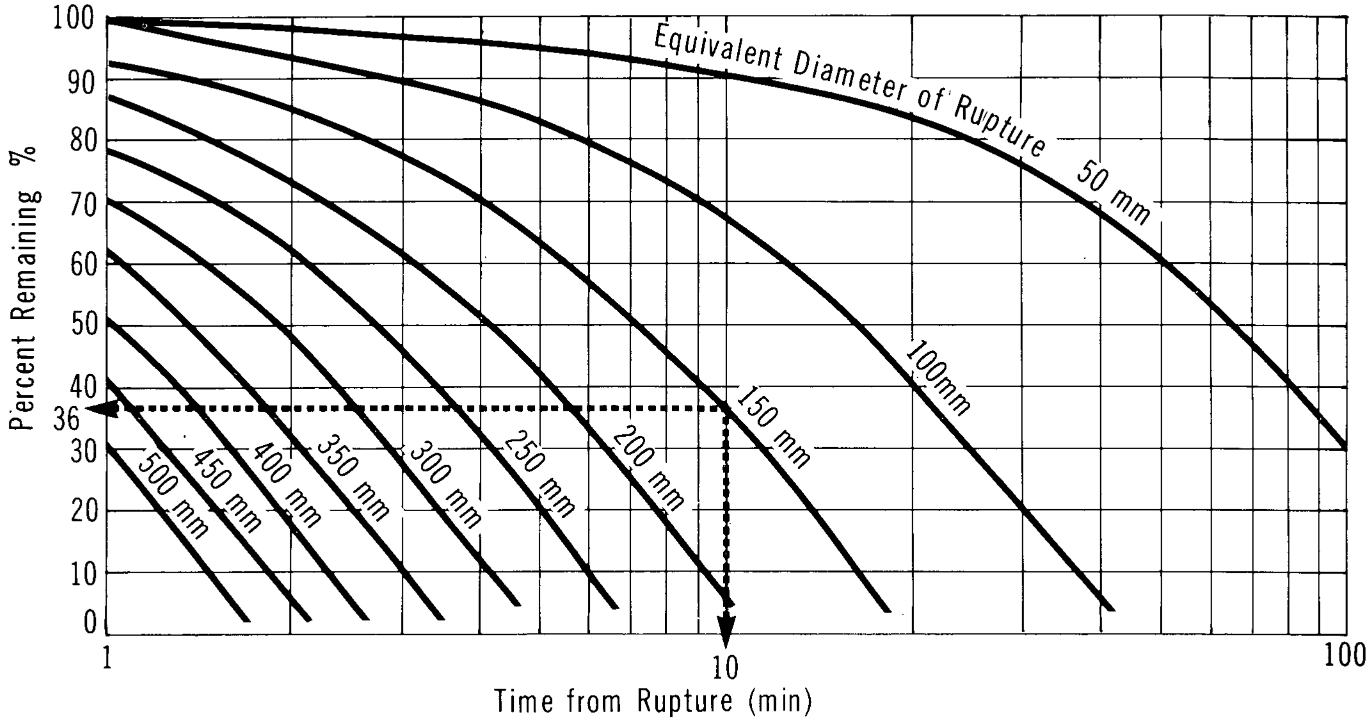
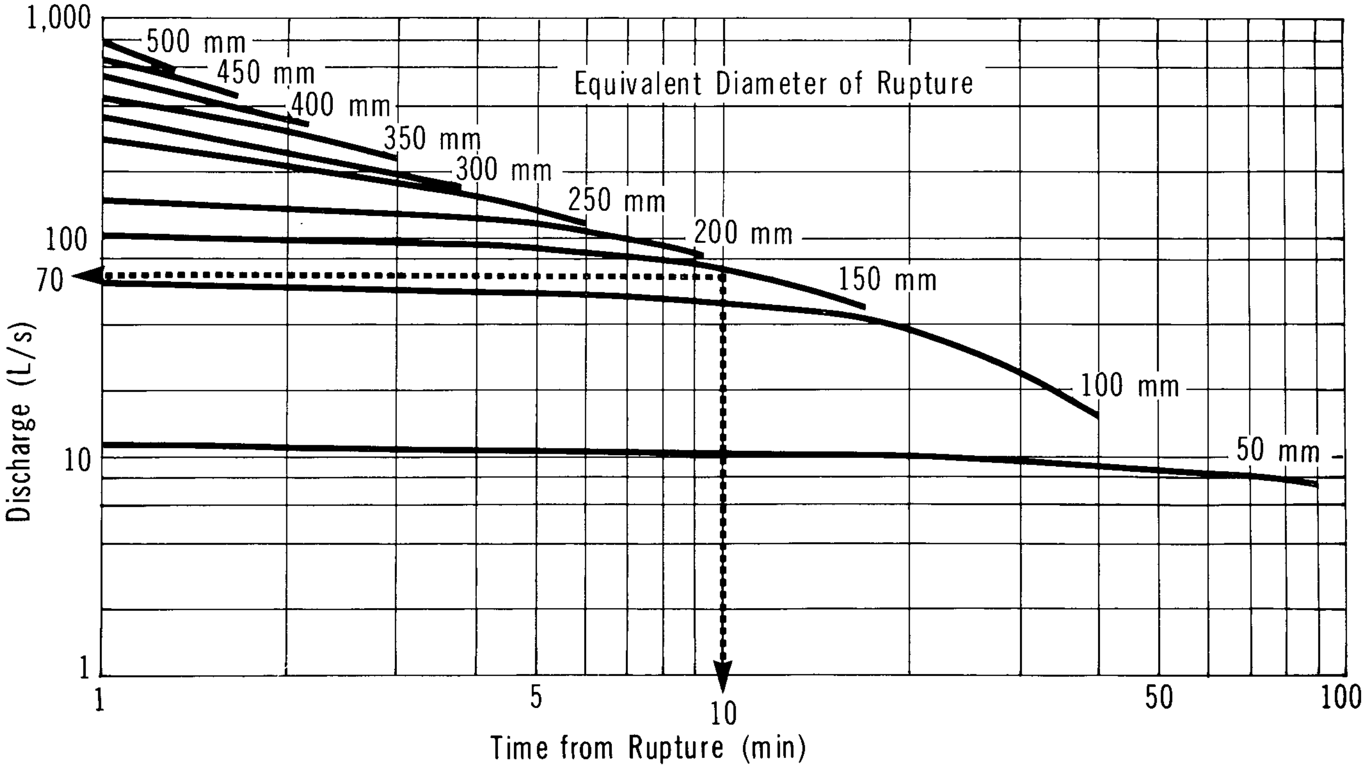


FIGURE 5

AMMONIUM PHOSPHATES

DISCHARGE RATE VS TIME



5.2.3 Sample Calculations.

i) Problem A

The standard tank car (2.75 m Ø x 13.4 m long), filled with an aqueous solution of ammonium phosphates, 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 4
- 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 5
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in Air

Because ammonium phosphates are nonvolatile, there is no significant potential for dispersion in air.

5.4 Behaviour in Water

5.4.1 Introduction. When spilled in water, ammonium phosphates 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 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. As ammonium phosphates are denser than water, the maximum concentration would be expected near the bottom.

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 7:	time versus distance for a range of average stream velocities
Figure 8:	hydraulic radius versus channel width for a range of stream depths
Figure 9:	diffusion coefficient versus hydraulic radius for a range of average stream velocities
Figure 10:	alpha* versus diffusion coefficient for various time intervals
Figure 11:	alpha versus delta* for a range of spill sizes
Figure 12:	maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 13:	volume versus radius for the hazard zone for a range of lake depths
Figure 14:	average concentration versus volume for the hazard zone for a range of spill sizes

The flow chart in Figure 6 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 7 through 12) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

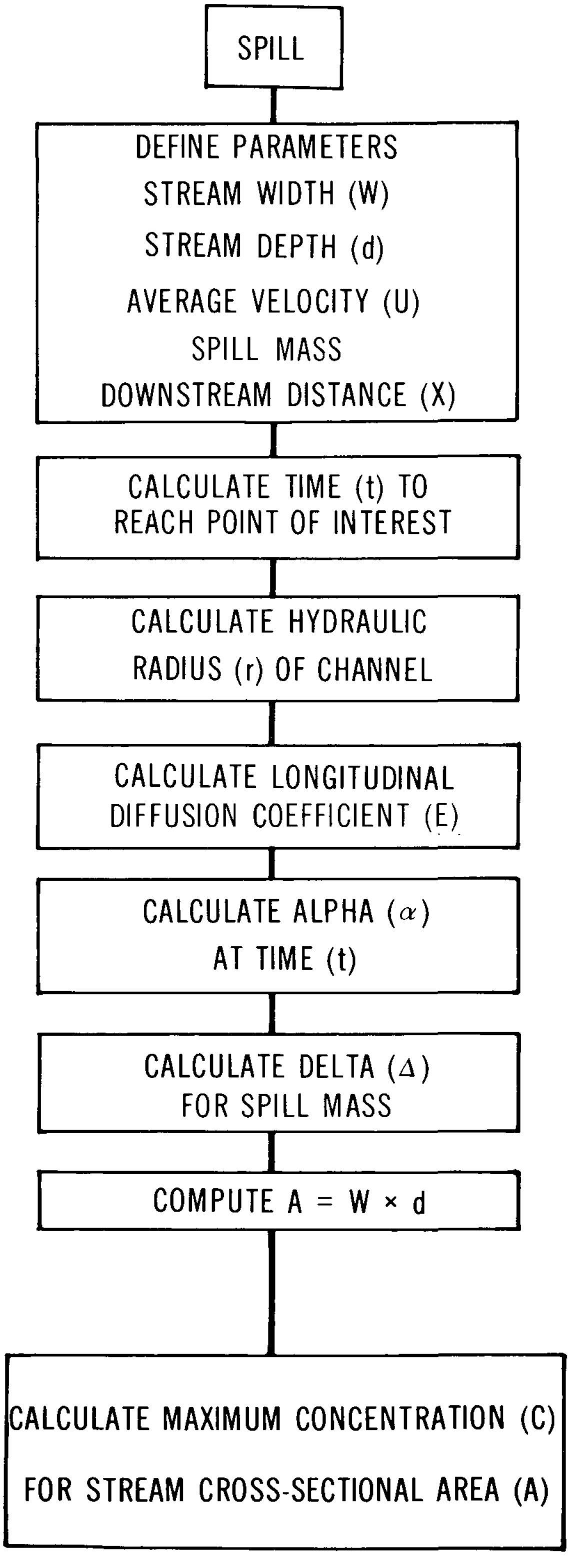
Figure 7: Time versus distance. Figure 7 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be readily obtained from Figure 7.

---

* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentrations.

FIGURE 6

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS



Step 1: Observed or Estimated

$W =$ ________ m

$d =$ ________ m

$U =$ ________ m/s

MASS = ________ tonnes

$X =$ ________ m

Step 2: Use Figure 7

$t =$ ________ minutes

Step 3: Use Figure 8

$r =$ ________ m

Step 4: Use Figure 9

$E =$ ________ m^2/s

Step 5: Use Figure 10

$\alpha =$ ________

Step 6: Use Figure 11

$\Delta =$ ________

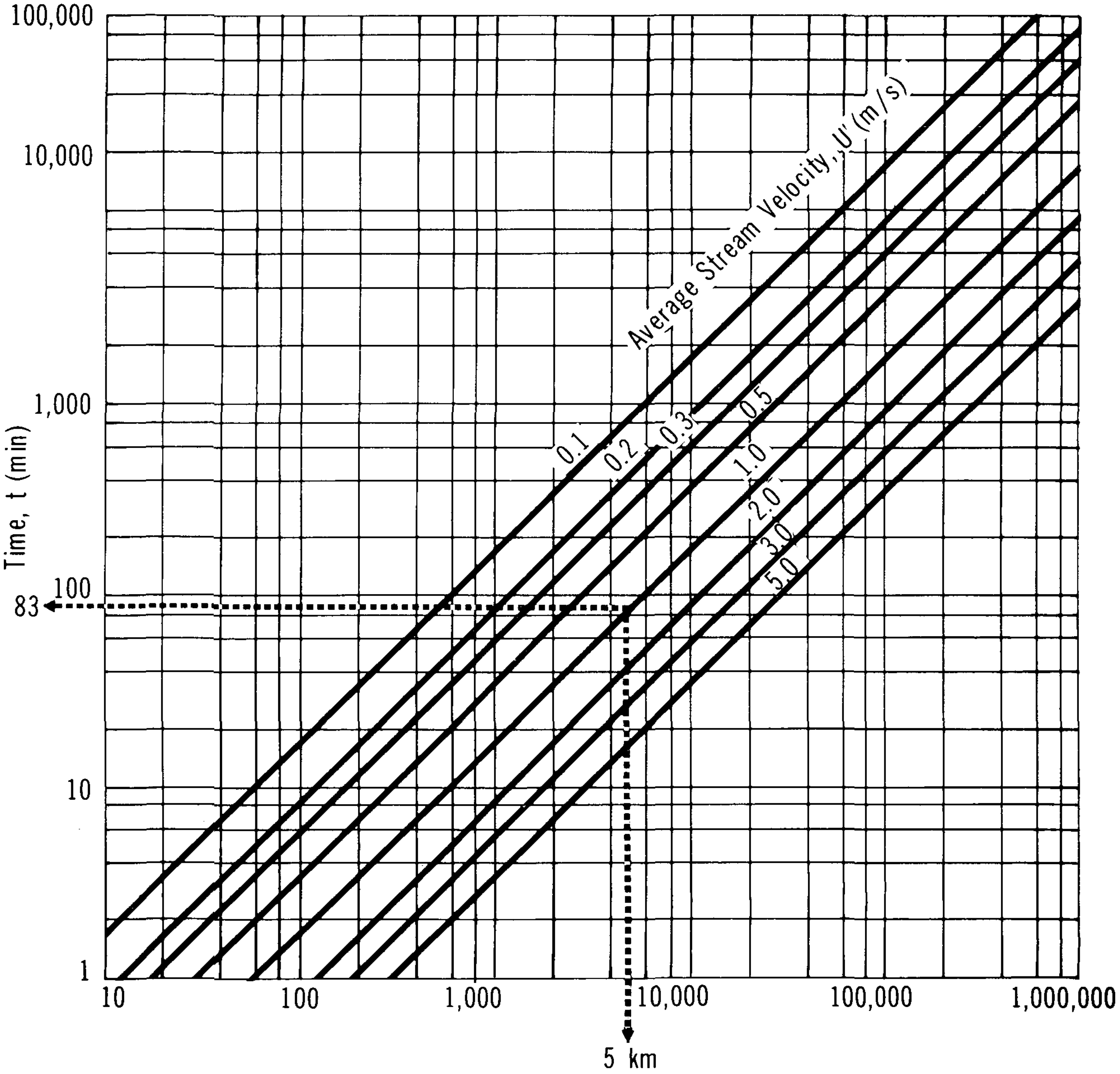
Step 7: Compute stream cross-sectional Area (A)

$A = W \times d$ _____ m^2

Step 8: Use Figure 12

$C =$ ________ ppm

TIME vs DISTANCE



Distance, X (m)

Figure 8: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentrations 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 8 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 9: Diffusion coefficient versus hydraulic radius. Figure 9 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 8 and the average stream velocity (U).

Figure 10: Alpha versus diffusion coefficient. Figure 10 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 11: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 11 to allow determination of pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 12: Maximum concentration versus delta. Figure 12 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 12 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 13: 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 13. The radius (r) represents the distance from the spill to the point of interest.

Figure 14: 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 14 for a known mass of spill. This assumes

FIGURE 8

HYDRAULIC RADIUS VS CHANNEL WIDTH

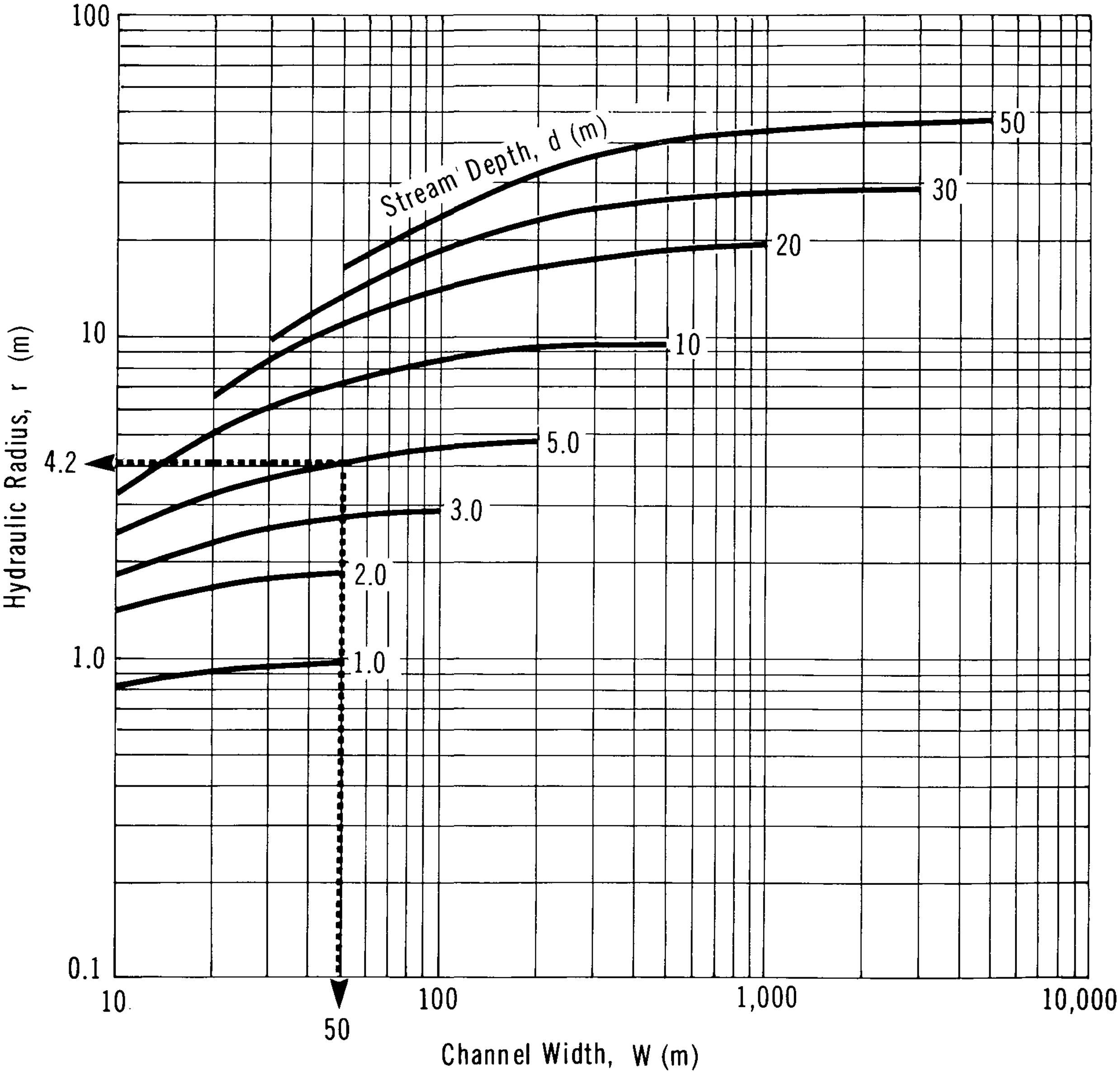
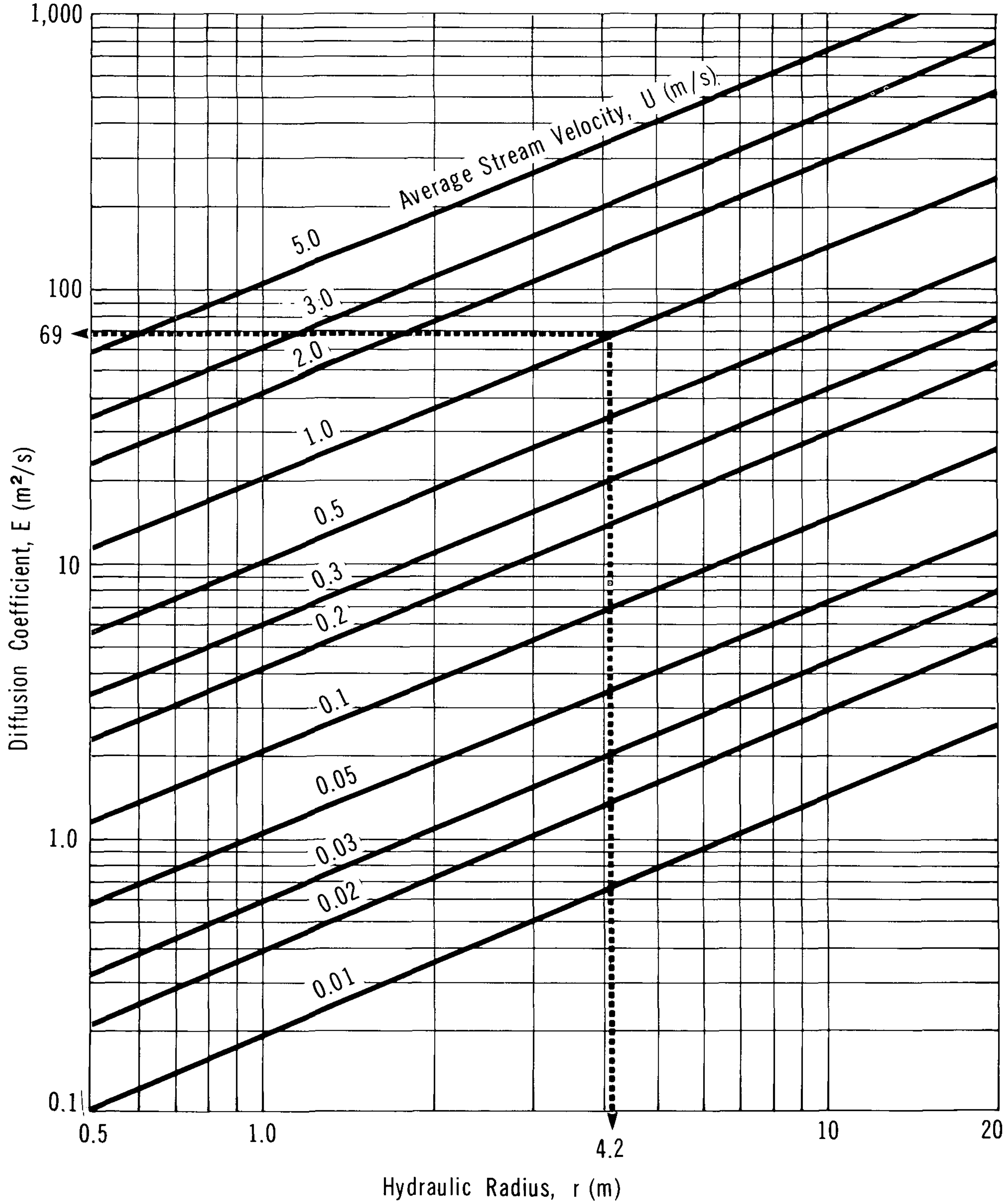


FIGURE 9

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS



ALPHA vs DIFFUSION COEFFICIENT

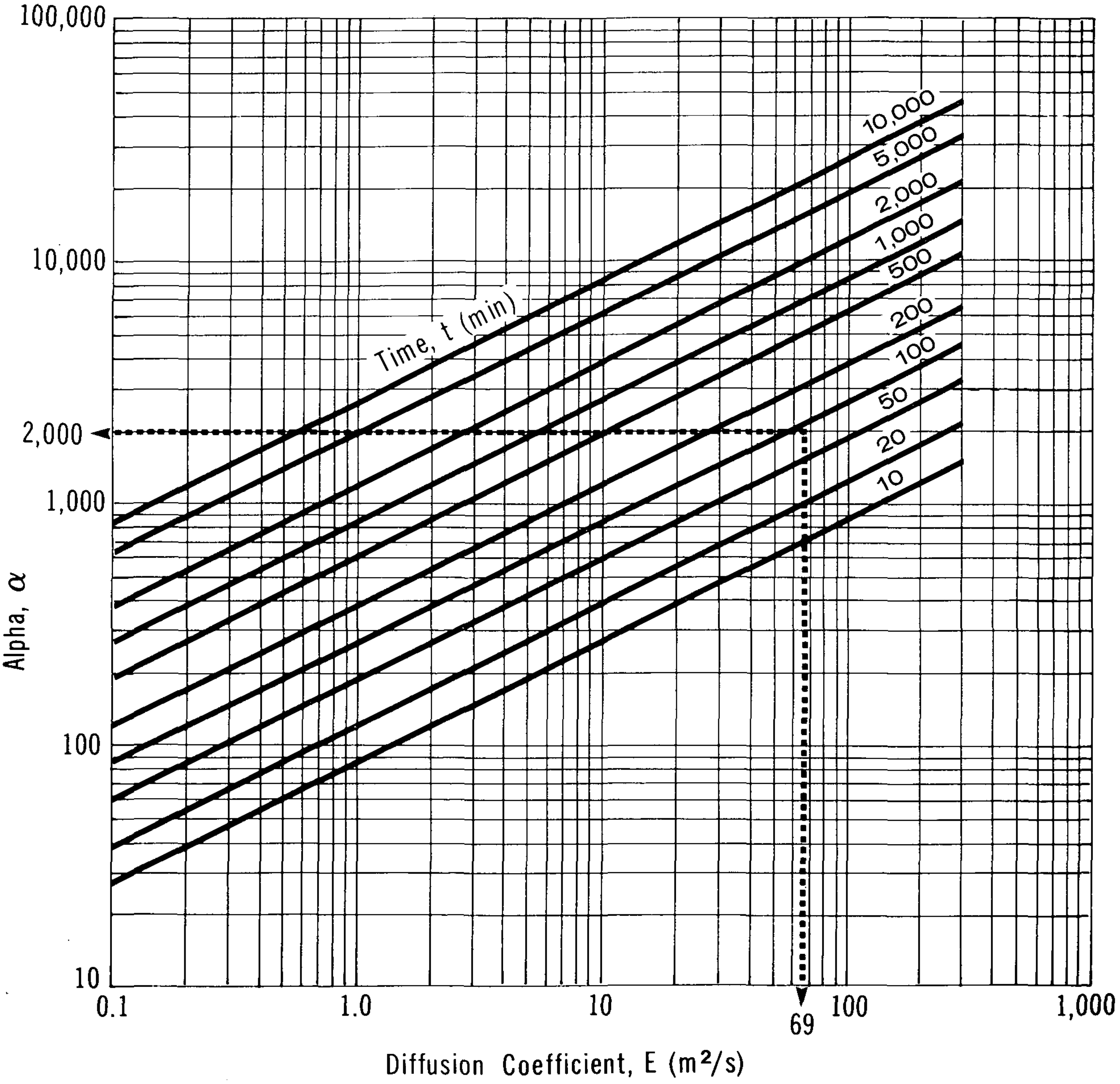
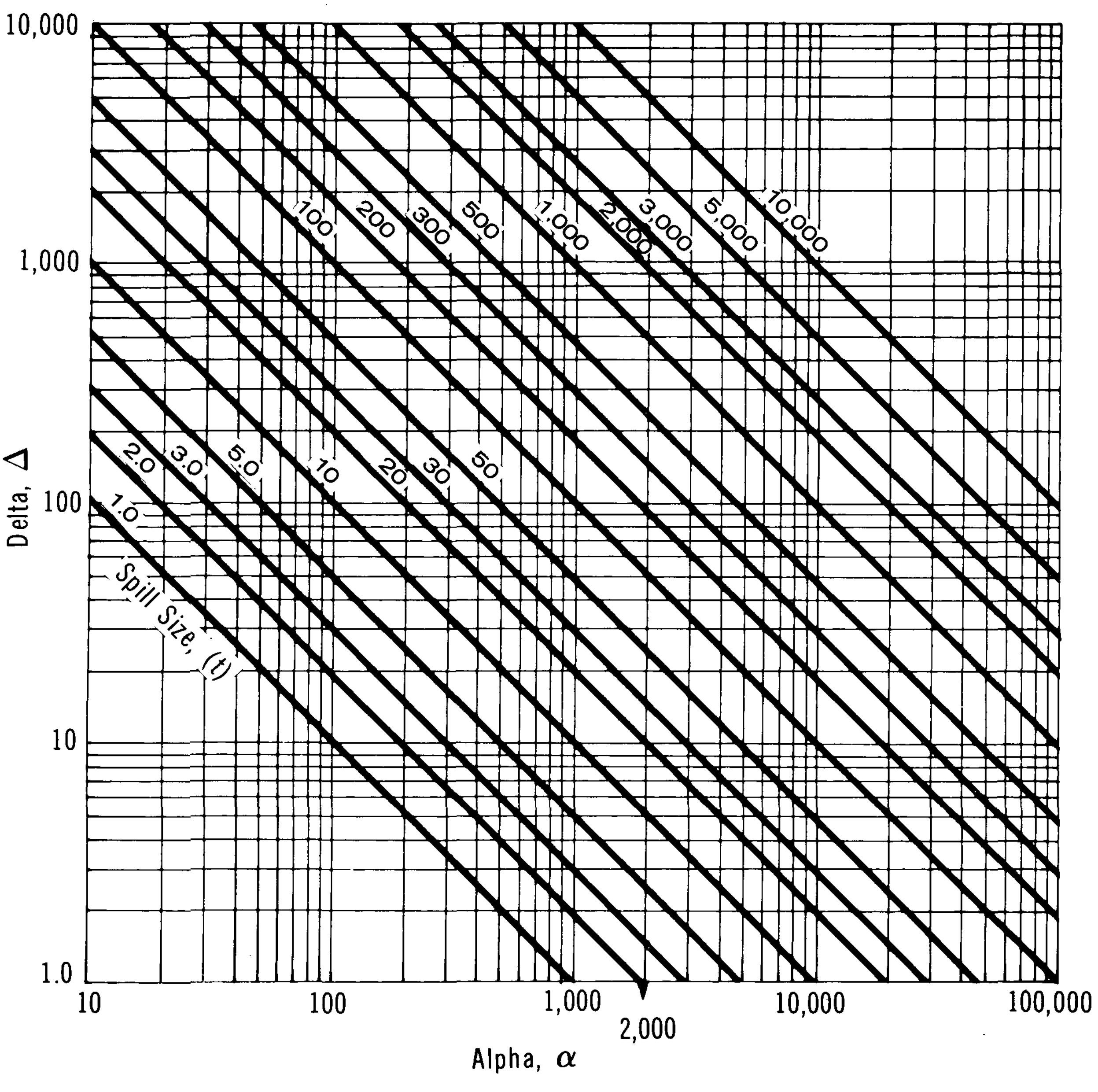


FIGURE 11

AMMONIUM PHOSPHATES

ALPHA vs DELTA



MAXIMUM CONCENTRATION vs DELTA

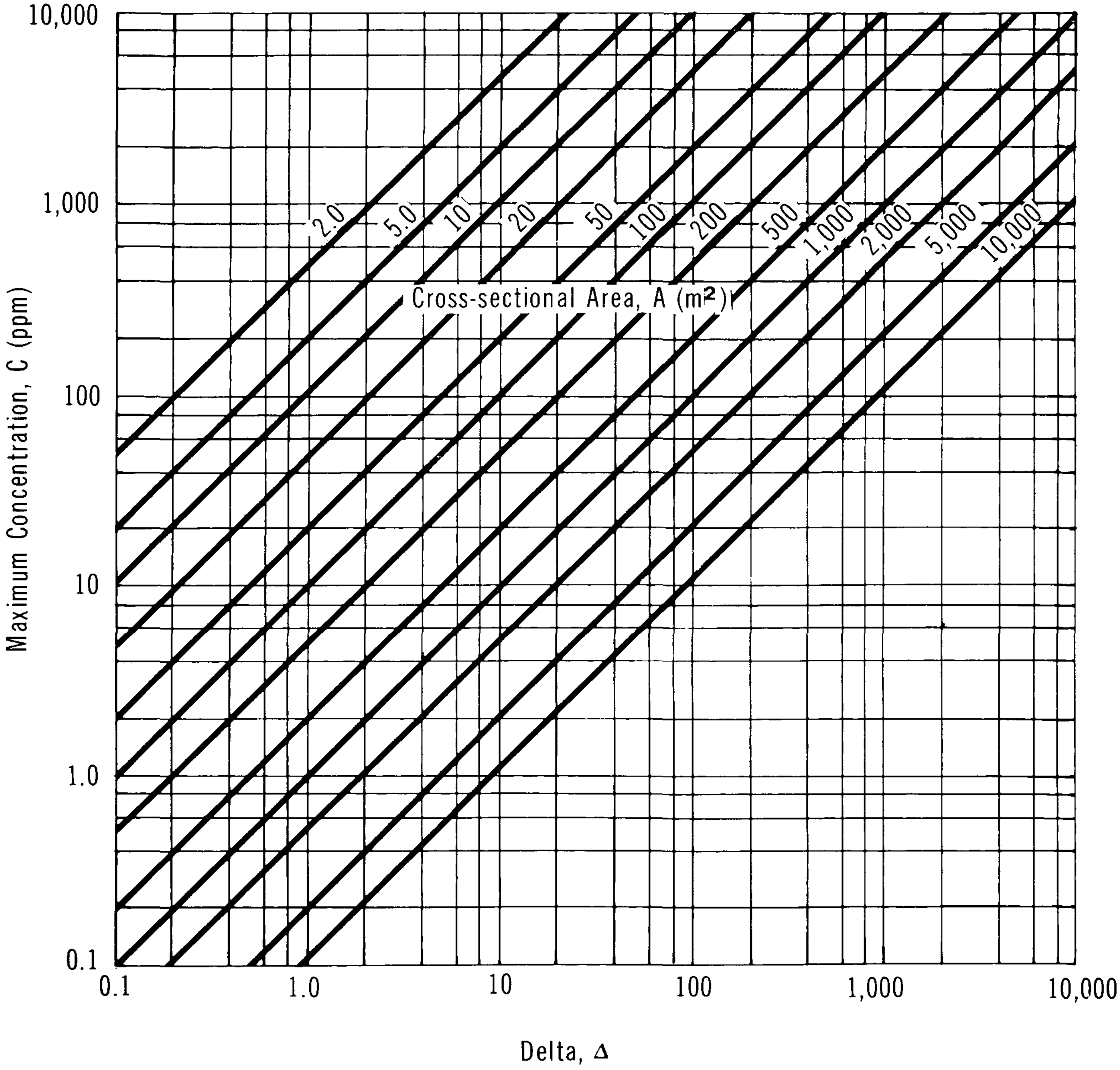
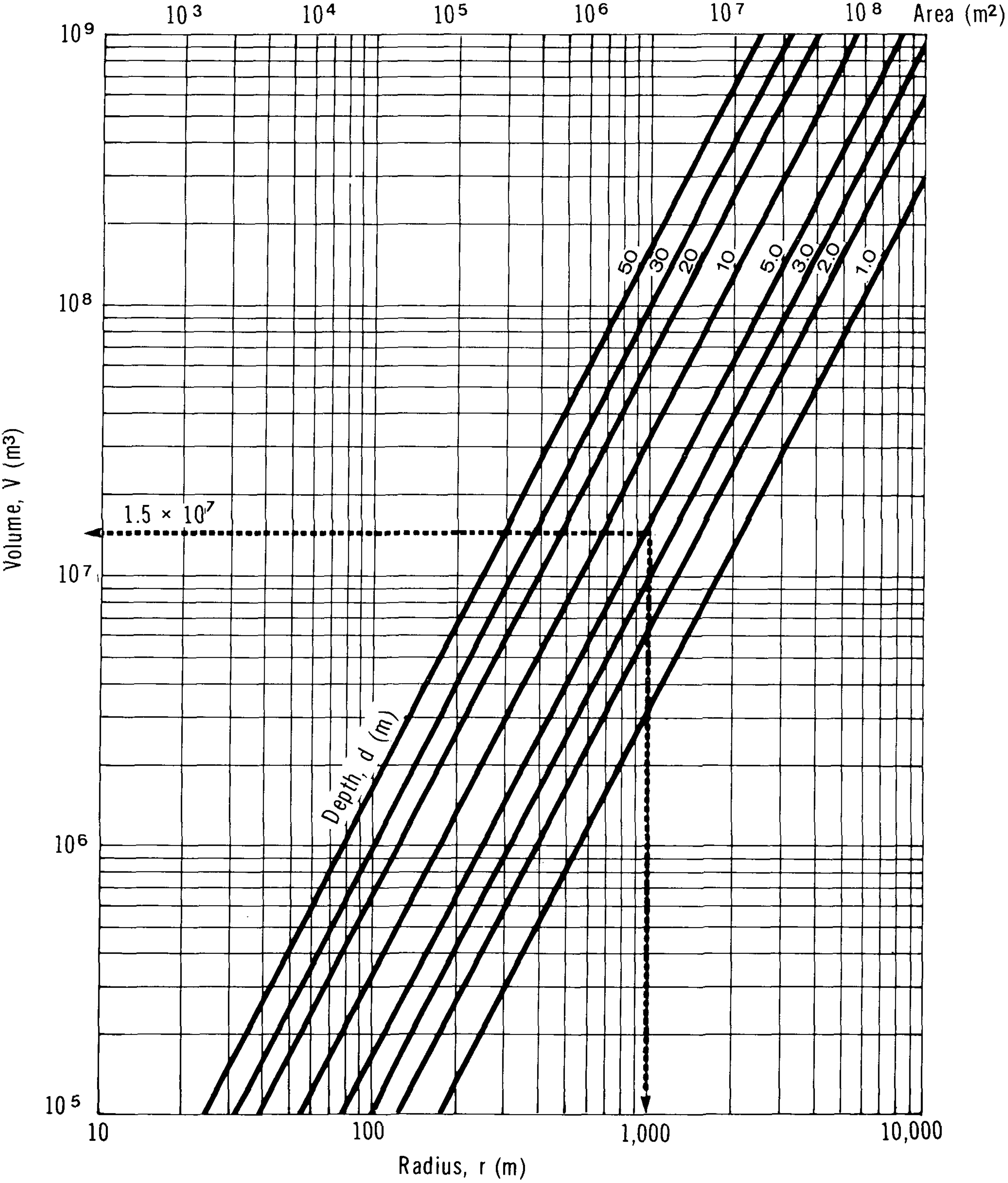


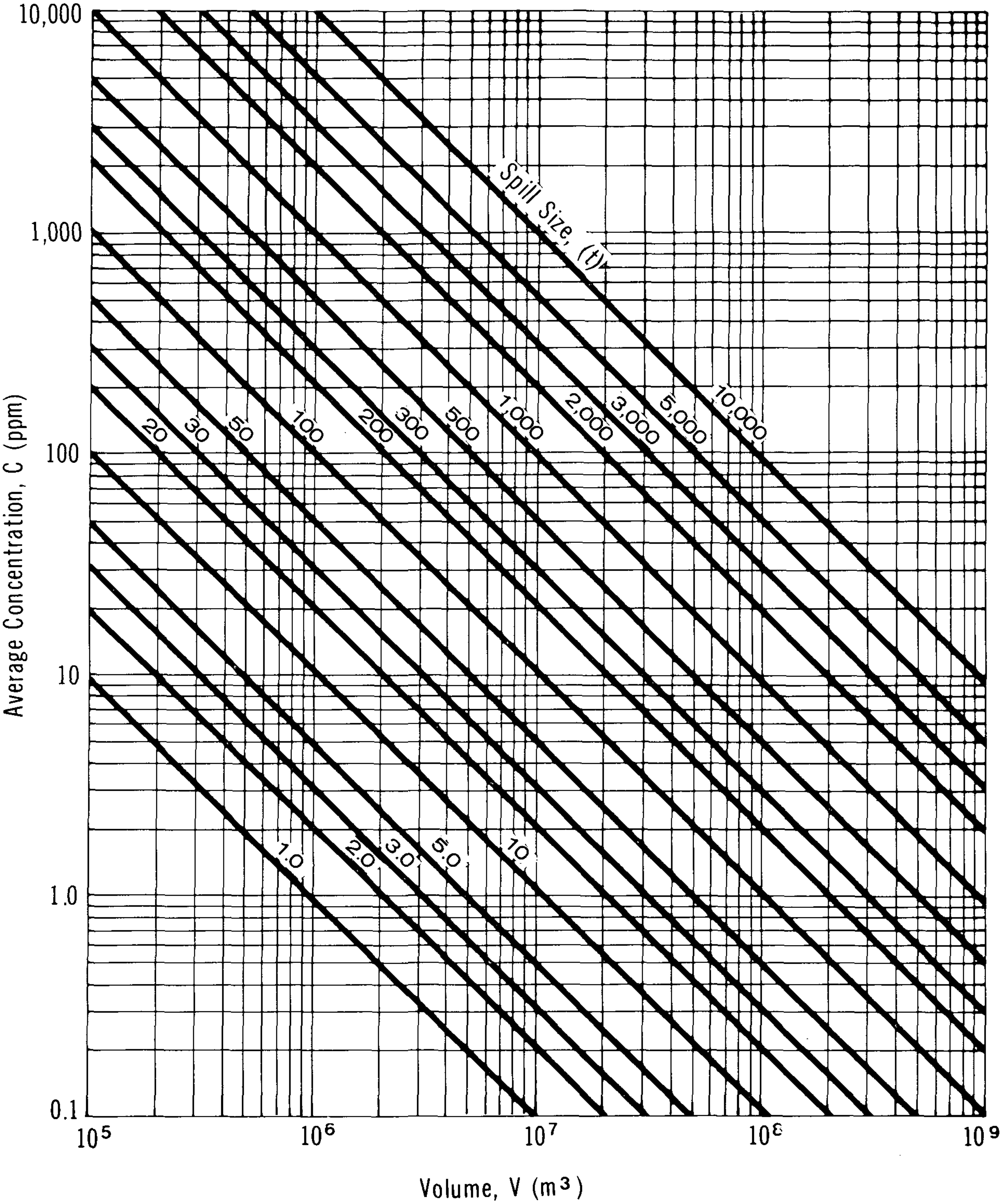
FIGURE 13

AMMONIUM PHOSPHATES

VOLUME vs RADIUS



AVERAGE CONCENTRATION vs VOLUME



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 20 tonne spill of 30 percent ammonium phosphates 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?

<u>Solution</u>

Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s
- mass = 20 tonnes of 30 percent solution, equivalent to 6 tonnes of 100 percent ammonium phosphates
- X = 5,000 m

Step 2: Calculate time to reach point of interest

- Use Figure 7
- With X = 5,000 m and U = 1 m/s, t = 83 min

Step 3: Calculate hydraulic radius (r)

- Use Figure 8
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate longitudinal diffusion coefficient (E)

- Use Figure 9
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 10
- With E = 69 m^2/s and t = 83 min, α = 2,000

Step 6: Calculate delta (Δ)

- Use Figure 11
- With alpha (α) = 2,000 and mass = 6 tonnes, delta (Δ) = 3

Step 7: Compute stream cross-sectional area (A)

- $A = W \times d = 50 \times 5 = 250\ m^2$

Step 8: Calculate maximum concentration (C) at point of interest

- Use Figure 12
- With $\Delta = 3$ and $A = 250\ m^2$, $C = 12$ ppm

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of 30 percent ammonium phosphates 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
- $r = 1{,}000$ m
- mass = 6 tonnes (equivalent)

Step 2: Determine the volume of water available for dilution or

- Use Figure 13
- With $r = 1{,}000$ m, $d = 5$ m, the volume is approximately $1.6 \times 10^7\ m^3$

Step 3: Determine the average concentration

- Use Figure 14
- With $V = 1.6 \times 10^7\ m^3$ and mass = 6 tonnes, the average concentration is 0.38 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 ammonium phosphates onto soil and their transport downward through the soil are presented here.

Ammonium phosphates are generally shipped and stored in solid form as monoammonium $[(NH_4)H_2PO_4]$ and/or diammonium $[(NH_4)_2HPO_4]$ phosphate. Only the diammonium salt will be considered here; however, similar characteristics for the monoammonium salt can be anticipated.

When the solid is spilled, only a limited groundwater pollution hazard exists if the soil is dry and cleanup occurs prior to precipitation. The solubility of $(NH_4)_2HPO_4$ at 20°C is approximately 69 g/100 mL. Thus, precipitation or water used to flush the site will create a solution of the contaminant which can infiltrate the soil.

Both ammonium and phosphate ions can interact with the soil extensively, primarily through ion exchange. However, this has not been accounted for here since the exchanged ions can also represent a contamination problem.

Runoff will occur under conditions of excess moisture. However, 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 move in the direction of groundwater flow. A contaminated plume will be produced, with diffusion and dispersion serving to reduce the concentration somewhat. This is shown schematically in Figure 15.

5.5.2 Equations Describing Diammonium Phosphate Movement into Soil. The equations and assumptions used to describe contaminant movement in solution 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 Diammonium Phosphate in Soil. The saturated hydraulic conductivity (K_o) in m/s is given by:

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

where: k = intrinsic permeability of the soil (m^2)

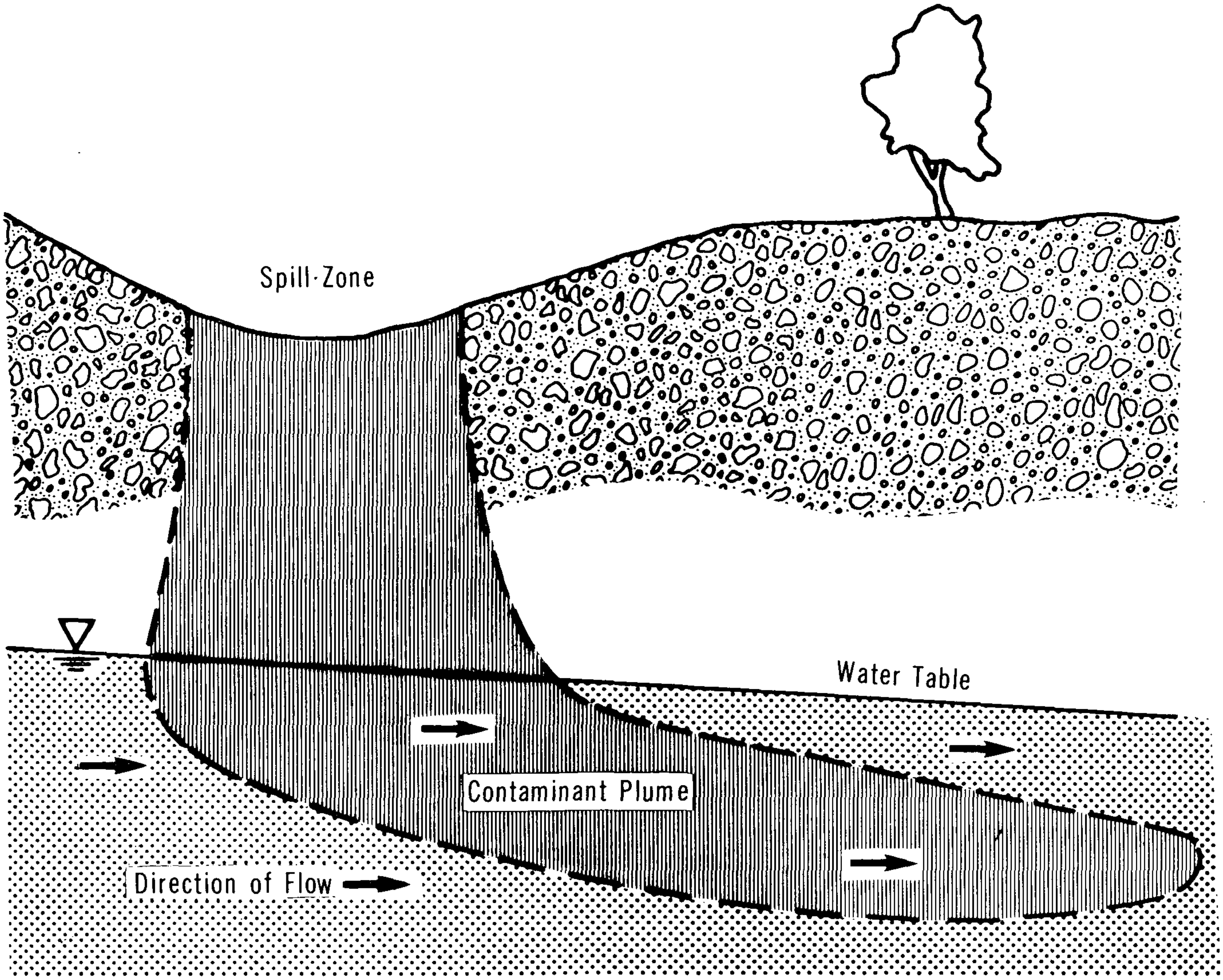
ρ = mass density of the fluid (kg/m^3)

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

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

The fluids involved are $(NH_4)_2HPO_4$, 30 percent by weight, representing a strong solution, and water. The water calculations represent the extreme as the solution is diluted.

SCHEMATIC SOIL TRANSPORT



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

Property	$(NH_4)_2HPO_4$, 30% 20°C	$(NH_4)_2HPO_4$, 30% 4°C	Water 20°C
Mass density (ρ), kg/m^3	1,151	1,154	998
Absolute viscosity (μ), Pa•s	2.6×10^{-3}	4.0×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(0.44 \times 10^7)k$	$(0.28 \times 10^7)k$	$(0.98 \times 10^7)k$

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

Property	Soil Type: Coarse Sand	Soil Type: Silty Sand	Soil Type: 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 (θfc), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of ammonium phosphates 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 16. The nomograms are presented as Figures 17, 18 and 19. The water line on the nomograms represents the maximum penetration of water at 20°C, in time t_p. It is a limiting condition as the solution becomes diluted with water.

5.5.6 Sample Calculation. A 20 tonne spill of $(NH_4)_2HPO_4$ as a solid has occurred on silty sand. The temperature is 20°C; the spill radius is 8.6 m. During cleanup, a rainfall occurs. Calculate the depth of penetration 10 days after the rainfall.

FIGURE 16

FLOWCHART FOR NOMOGRAM USE

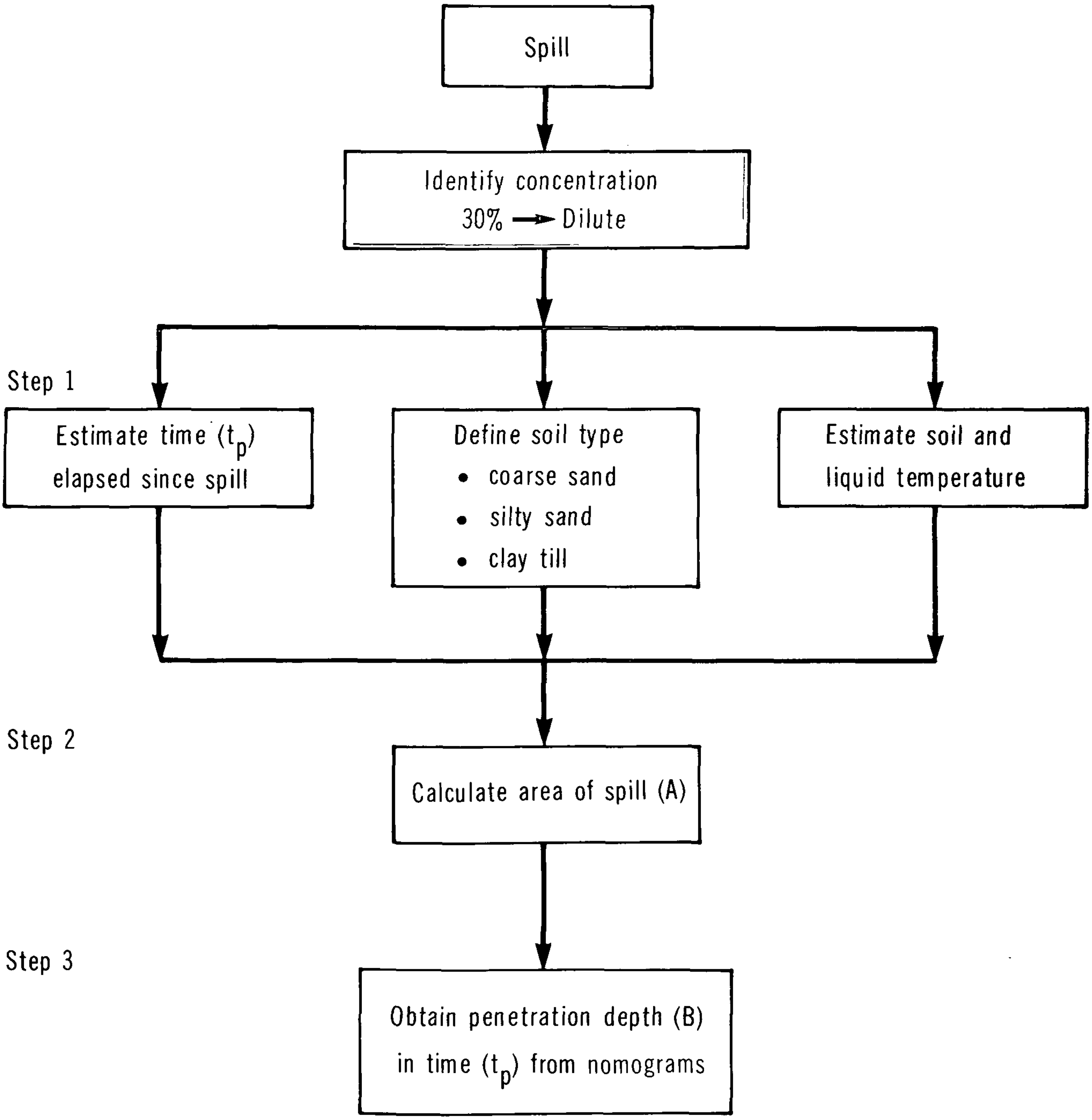
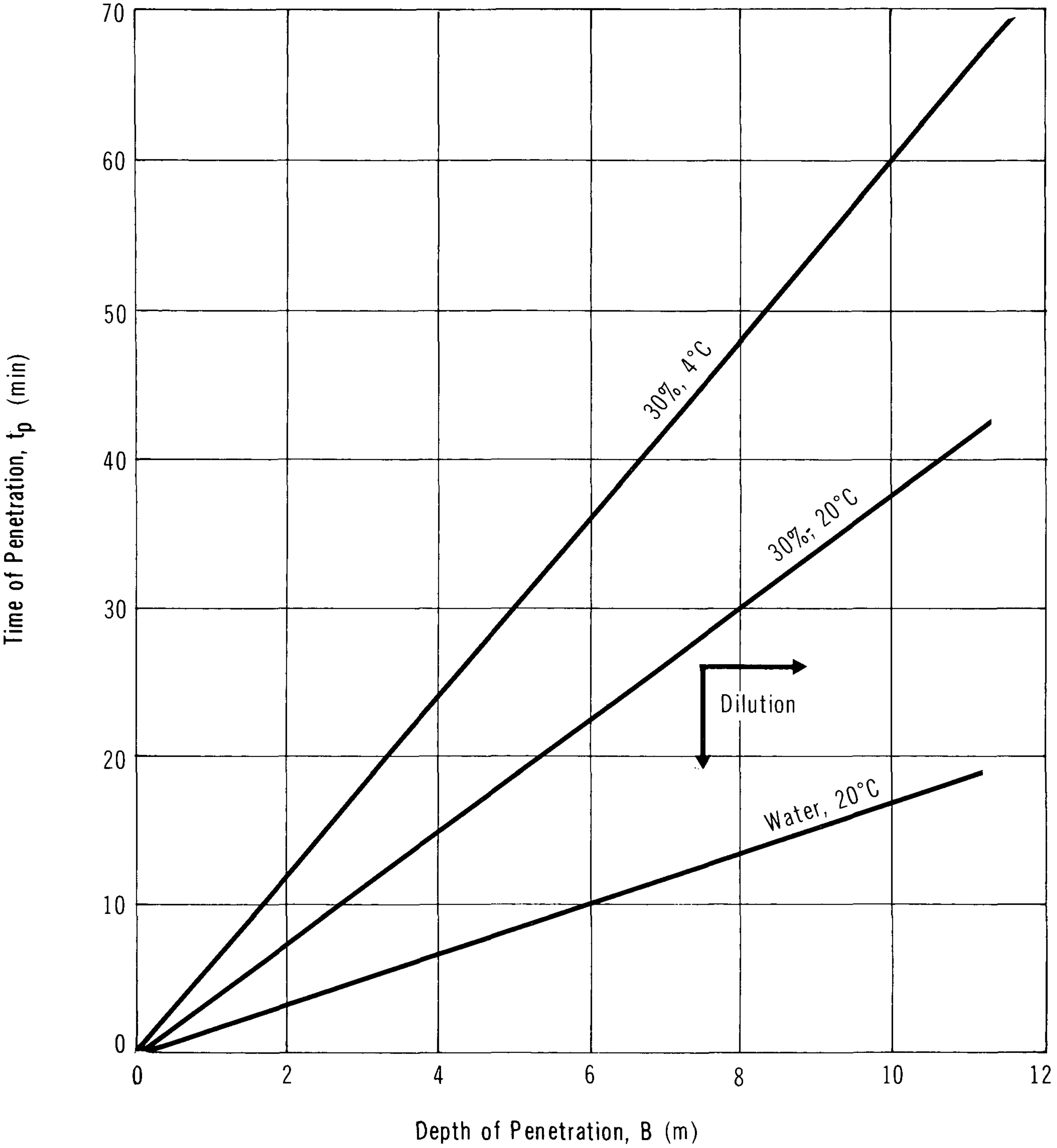


FIGURE 17

AMMONIUM PHOSPHATES

PENETRATION IN COARSE SAND



PENETRATION IN SILTY SAND

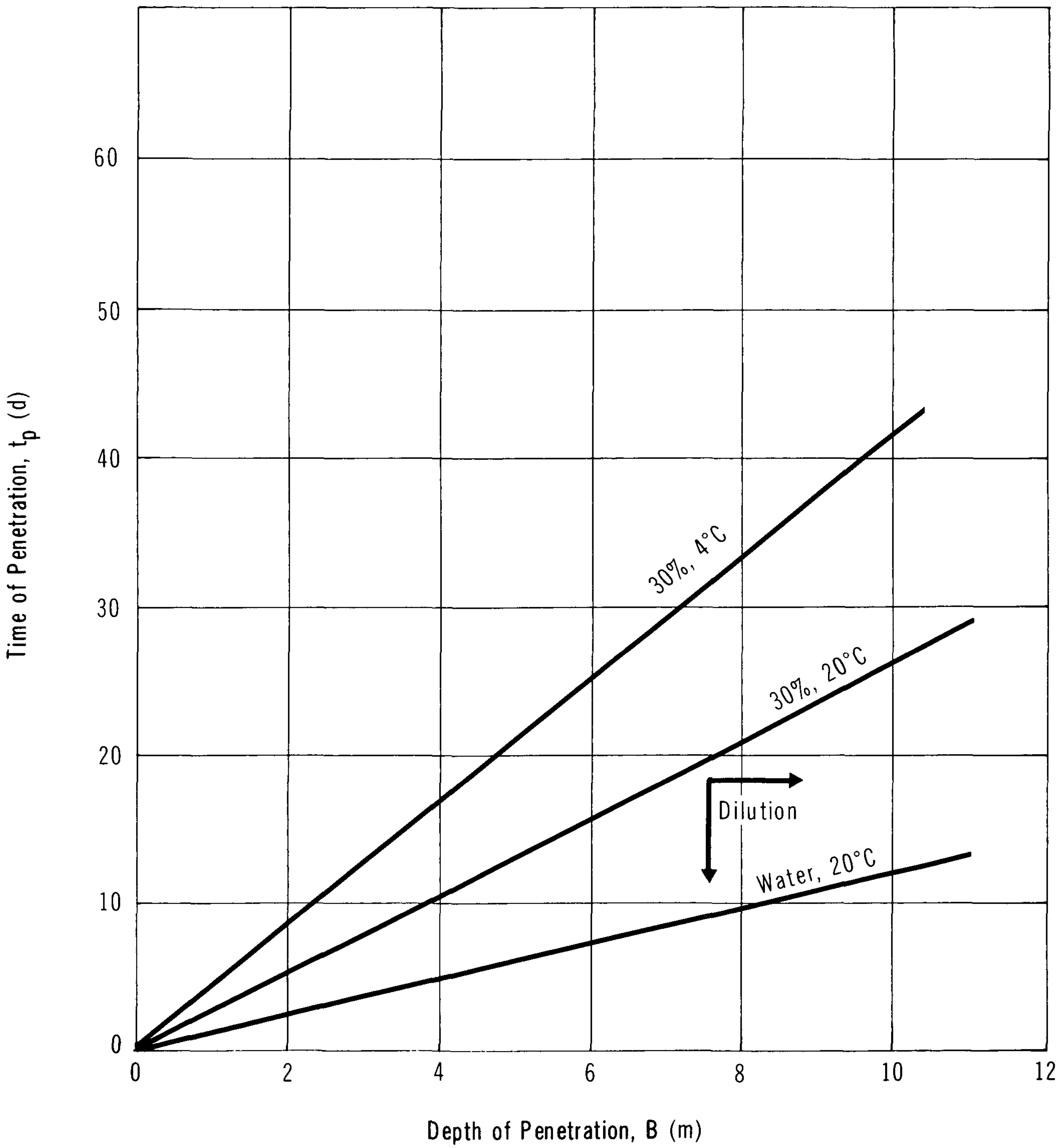
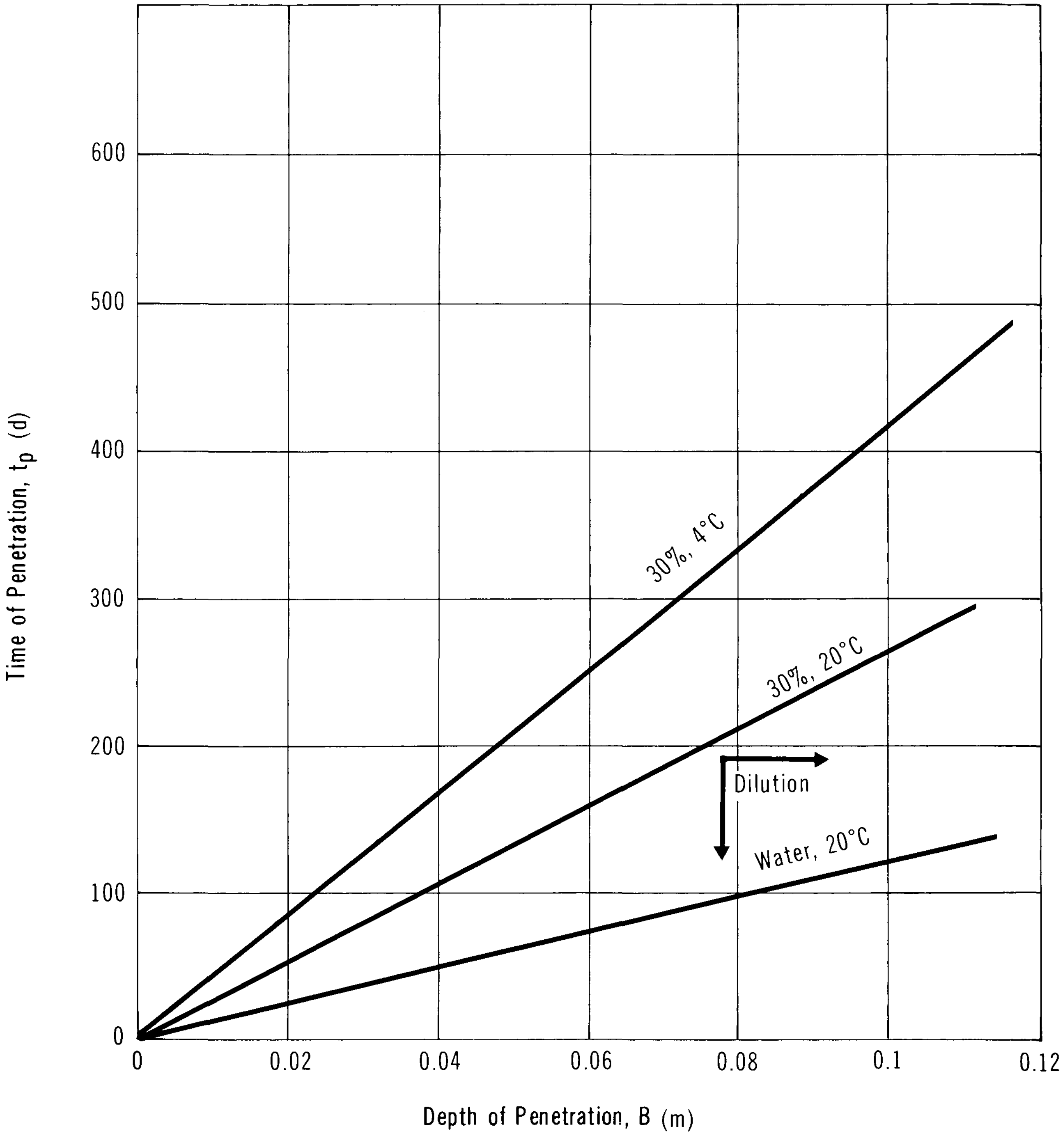


FIGURE 19

PENETRATION IN CLAY TILL



Solution

Step 1: Define parameters

- 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_p) = 10 days

Step 2: Calculate area of spill

- $A = \pi r^2 = 232\ m^2$

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

- For silty sand, t_p = 10 days
- Penetration depth from Figure 18 is:

30%	Dilute (water, worst condition)
B = 3.9 m	B = 8.3 m

- Groundwater table has not been reached.

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Ontario recommends a limit of 0.02 mg/L of unionized ammonia (Water Management Goals 1978); 0.05 mg/L has been recommended in the United States (OHM-TADS 1981; O.I. 1970).

6.1.2 Air. Although both ammonia and phosphoric acid exposures or concentrations are regulated in various jurisdictions, ammonium phosphates levels are not. Hazards from ammonium phosphates are largely related to their decomposition or dissociation products, ammonia and phosphoric acids. These may be present if ammonium phosphates and bases come into contact with each other. Ontario's environmental ammonia concentration limit is 3.6 mg/m^3; the limit for phosphoric acids is 100 µg/m^3 (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Ammonium phosphates have been assigned a TL_m96 (4-day median lethal toxicity rating) of 1,000 to 100 mg/L (RTECS 1979).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxicity Tests					
145	96	Salmon fry	LC_{50}		Johnson 1977
94	96	Trout fry	LC_{50}		Johnson 1977
350	96	Bluegill	LC_{50}		Johnson 1977
450	96	Largemouth bass	LC_{50}		Johnson 1977
225	24	Fathead minnow	LC_{50}	pH 7.8; static & dynamic bioassays	Inman 1974
155	96	Fathead minnow	LC_{50}	pH 7.8; static & dynamic bioassays	Inman 1974
Invertebrates					
40	96	Scud	LC_{50}		Johnson 1977

6.2.3 Aquatic Studies. The threshold concentration for fish is 0.5 mg/L free ammonia. Toxicity is related directly to the level of unionized ammonia (OHM-TADS 1981).

6.3 Effect Studies (OHM-TADS 1981)

Ammonium phosphates are nutrients and can stimulate algal blooms.

6.4 Degradation

Ammonium phosphates are nutrients; both the nitrogen and phosphorus are readily assimilated by microorganisms. Chlorination of water containing ammonium salts, however, causes the formation of odorous chloramines (OHM-TADS 1981).

6.5 Long-term Fate and Effects

As nutrients, ammonium phosphates spills may alter species population balances. There is no potential for bioaccumulation or food chain contamination (OHM-TADS 1981).

7 HUMAN HEALTH

There is a very limited amount of information in the literature concerning the toxicological effects of test animal and human exposures to ammonium phosphates. Much of the published information pertaining to the health effects of these chemicals deals with their irritant effects on the eyes and skin.

There was no information in the literature on the effects of ammonium phosphates on reproduction, nor on their mutagenicity or carcinogenicity. No information was encountered on the effects of chronic exposures to these chemicals.

Dibasic ammonium phosphate and monobasic ammonium phosphate have been reported in the EPA TSCA inventory. The data summarized here are representative of information in the literature.

7.1 Recommended Exposure Limits

Established exposure standards for ammonium phosphates were not encountered in the published literature or in Canadian provincial legislation.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
No data			
Short-term Exposure Limits (STEL)			
No data			
Provisional Limit			
(Time not specified)		0.5 mg/m^3 (in air)	GE 1980
Other Human Toxicities			
No data			

7.2 Irritation Data

7.2.1 Skin Contact. No data

7.2.2 Eye Contact. No data

7.3 Threshold Perception Properties

7.3.1 Odour. No data

Dibasic ammonium phosphate	-	Odour Characteristics:	Faint ammonia odour (CHRIS 1978) Odourless (ERCO PDS 1981b)
Monobasic ammonium phosphate	-	Odour Characteristics:	Faint acid odour (CHRIS 1978) Odourless (ERCO PDS 1981a)

7.3.2 Taste. No data

7.4 Long-term Studies

7.4.1 Inhalation. No data

7.4.2 Ingestion. No data

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. Dust may cause coughing or difficult breathing.
2. Monoammonium form causes irritation of mucous membranes (CHRIS 1978).
3. Chest pains (TDB (on-line) 1981).
4. Dyspnea (TDB (on-line) 1981).
5. Severe irritation results in hypoxemia (TDB (on-line) 1981).
6. Diammonium form can cause pulmonary edema and asphyxia (CHRIS 1978).

7.5.2 Ingestion.

1. Corrosion of mucous membranes of mouth, throat, and esophagus, with immediate pain (TDB (on-line) 1981).
2. Dysphagia (TDB (on-line) 1981).
3. Epigastric pain, which may be associated with nausea and vomiting of mucoid and "coffee ground" material (TDB (on-line) 1981).
4. Gastric pain (TDB (on-line) 1981).
5. Circulatory collapse which may lead to renal failure (TDB (on-line) 1981).

6. Clammy skin (TDB (on-line) 1981).
7. Weak and rapid pulse (TDB (on-line) 1981).
8. Shallow respiration (TDB (on-line) 1981).
9. Scanty urine (TDB (on-line) 1981).
10. Circulatory shock (TDB (on-line) 1981).
11. Tachycardia (TDB (on-line) 1981).
12. Glottic edema (TDB (on-line) 1981).
13. Late esophageal, gastric and pyloric strictures and stenoses which may require major surgical repair (TDB (on-line) 1981).
14. Death (TDB (on-line) 1981).

7.5.3 Skin Contact.

1. Mild skin irritation (GE 1980).
2. Dermatitis (TDB (on-line) 1981).
3. Roughened skin (TDB (on-line) 1981).
4. Severe burns (TDB (on-line) 1981).

7.5.4 Eye Contact.

1. Irritation (CHRIS 1978).
2. Severe pain (TDB (on-line) 1981).
3. Swelling (TDB (on-line) 1981).
4. Corneal erosion (TDB (on-line) 1981).
5. Blindness (TDB (on-line) 1981).

7.6 Human Toxicity to Decay or Combustion Products

Irritating fumes of ammonia, phosphorus oxides and oxides of nitrogen may form in fires (CHRIS 1978). Upon heating, ammonium phosphates give off toxic gases of nitrogen oxides (GE 1980). The fumes of ammonia and phosphorus oxides would be of primary concern.

7.6.1 Nitric Oxide, Nitrogen Dioxide, Nitrogen Tetroxide and Ammonia. Nitric oxide is a colourless gas with a sharp, sweet odour. It combines with hemoglobin which is oxidized in the blood to methemoglobin, with resulting anoxia. Nitric oxide is only slightly irritating to the upper respiratory tract and eyes; therefore, dangerous amounts of fumes may be inhaled before any discomfort is noticed (Sax 1968). In air, nitric oxide is oxidized to nitrogen dioxide which is four to five times as toxic as nitric oxide (Patty 1963). The TLV® for nitric oxide is 25 ppm (8 h - TWA) and 35 ppm (STEL) (TLV 1981).

At normal environmental temperatures, nitrogen dioxide and nitrogen tetroxide are always found together (proportion of NO_2 to N_2O_4 at 37.5°C is 3:7) (Sax 1968). At higher temperatures, the proportion of NO_2 increases. Mixtures are often referred to as "nitrogen dioxide", which is dark brown with a pungent, acrid odour. Nitrogen dioxide is mildly irritating to the eyes, nose and upper respiratory mucosa; therefore, dangerous amounts of fumes may be inhaled before any discomfort is noticed. Nitrogen dioxide is slightly soluble in water, reacting in the presence of oxygen to form nitric and nitrous acids. These acids are formed deep in the respiratory system where they irritate the lungs, causing congestion of the throat and bronchi, and edema of the lungs. Symptoms of exposure include weakness, nausea, abdominal pain, coughing, mucoid frothy sputum, accelerated heart action, severe cyanosis, and convulsions. Excessive exposure will result in death.

Immediate symptoms may clear up on breathing fresh air; however, the above symptoms may ensue in 6 to 24 hours. In fatal cases, death occurs within 8 to 48 hours following exposure. The TLV® for NO_2 is 3 ppm (8 h - TWA) (TLV 1981) and 5 ppm (STEL). There is no TLV® for nitrogen tetroxide.

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 35 ppm (STEL) (TLV 1981).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Ammonium Phosphate (Monobasic) with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
<u>SPECIAL CHEMICALS</u>														
Sodium Hypochlorite						x								NFPA 1978
Sodium Chlorate						x								GE 1980
<u>GENERAL CLASSES OF SUBSTANCES</u>														
Bases						x		x					Release of ammonia	GE 1980

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

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

9.1.1 Fire Concerns. Ammonium phosphates are noncombustible materials; however, in a fire they may decompose, liberating irritating ammonia fumes, oxides of nitrogen, and phosphates. They can also polymerize upon heating, again liberating ammonia (Stauffer PSIS 1981).

9.1.2 Fire Extinguishing Agents. Use water, dry chemical, CO_2, foam or other suitable suffocation agents (Stauffer PSIS 1981).

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 inhalation.

9.1.3.2 Spills on land. Sweep up the spilled material, being careful not to create dust, and place sweepings into an appropriate chemical waste container for disposal (Stauffer PSIS 1981).

9.1.3.3 Spills on water. When spilled on water, the materials will dissociate and produce phosphate and ammonium ions. In situ treatment agents for phosphate ions are Al^{3+}, Ca^{2+}, Fe^{3+}, Mg^{2+}. Ammonium ions can be absorbed by natural zeolites or clinoptilolite (natural zeolite) (OHM-TADS 1981).

9.1.4 Disposal. Waste ammonium phosphates must never be discharged directly into sewer or surface waters. Following treatment either at the spill site or at a waste management facility, the resultant sludge can be disposed of in a secure landfill.

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 an ammonium phosphate:

- Impervious clothing, full facepiece and self-contained breathing apparatus should be worn if ammonia is present (Stauffer PSIS 1981).
- Rubber or plastic is recommended for gloves and boots (ERCO PDS 1981a).
- Chemical safety glasses should also be worn for eye protection in situations requiring this (ERCO PDS 1981a).

9.1.6 Special Precautions. Do not store in or near areas where mixing with sodium hypochlorite and certain other bases can occur as the liberation of ammonia may take place. Do not store in excessively hot areas (U.S. DOL MSDS 1979).

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 the criteria are included, and thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.1 Tank Spill (PC DOC 1982; HMIR 1980)

Vandalism at a fertilizer plant caused a 113,550 L tank containing liquid ammonium phosphates (7 percent ammonia) to spill its contents. Approximately 37,850 L of the product were collected in a catch basin while 75,000 L flowed into a nearby watercourse. Nearly 31,000 fish were reported dead from the mishap. Response personnel arrived a few days later and collected the remaining viscous material in the catch basin along with contaminated soil using backhoes, and disposed of such in a nearby farmer's field. Ammonia levels up to 60 mg/L were measured in the river near the spill site. The ammonia decreased to less harmful concentrations at approximately 2.5 km downstream from the spill.

It was concluded that with the next heavy rainfall, the ammonia in the river would be diluted to trace levels before reaching the river section used for drinking and recreation purposes, about 110 km downstream. No other fish kills were reported after the incident.

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 Ammonium Phosphates in Air

11.1.1 Colourimetric (AWWA 1981). This method is useful for concentrations of ammonium phosphates greater than 0.2 ppm or 851 $\mu g/m^3$ in air when a volume of 30 L of air is sampled.

A volume of air equal to 30 L is drawn through 0.8 µm pore size 37 mm diameter cellulose-ester filters. The sample is desorbed in 100 mL of water by shaking vigorously for 45 minutes. The extract should be free from colour and turbidity. One drop of phenolphthalein indicator is added. If the extract turns pink, strong acid is added drop-wise to discharge the colour. Ammonium molybdate reagent is prepared by dissolving 25 g ammonium molybdate in 175 mL water. This is added to a solution of 280 mL concentrated sulphuric acid in 400 mL water and diluted to 1 L. Stannous chloride reagent is prepared by dissolving 2.5 g stannous chloride in 100 mL glycerol and heating to dissolve. Molybdate reagent, 0.4 mL, plus 0.5 mL stannous chloride reagent are added to the extract. The temperature must be held constant within 2°C in the range of 20 to 30°C during colour development. The colour is read after 10 to 12 minutes at 690 nm using a suitable spectrophotometer. The absorbance is compared with a calibration curve, using a distilled water blank. In addition, a reagent blank must be run. The timing is critical because the colour develops progressively and later fades.

11.2 Qualitative Method for the Detection of Ammonium Phosphates in Air

The sample is collected as in Section 11.1.1, desorbed, then diluted with 6 mL of deionized water. A 1 mL volume of sample is transferred to a beaker. A 5 mL volume of concentrated nitric acid is added and the solution evaporated to approximately 1 mL. This should be done in a fume hood. A 2 mL volume of water is added and the solution transferred to a test tube. A 1 mL volume of 1 M ammonium nitrate and 2 mL of 0.5 M ammonium molybdate are added to the test tube. The contents are then heated to boiling. A yellow precipitate indicates the presence of phosphate (Welcher 1955).

11.3 Quantitative Method for the Detection of Ammonium Phosphates in Water

11.3.1 Colourimetric (AWWA 1981). This method is useful for concentrations of ammonium phosphates greater than 25 µg/L (0.025 ppm) in water.

A representative water sample, about 1 L, is collected. The sample should be free from colour and turbidity. One drop of phenolphthalein indicator is added. If the extract turns pink, strong acid is added drop-wise to discharge the colour. Ammonium molybdate reagent is prepared by dissolving 25 g ammonium molybdate in 175 mL water. This is added to a solution of 280 mL concentrated sulphuric acid in 400 mL water and diluted to 1 L. Stannous chloride reagent is prepared by dissolving 2.5 g stannous chloride in 100 mL glycerol and heating to dissolve. Molybdate reagent, 0.4 mL, plus 0.5 mL stannous chloride reagent are added to the extract. The temperature must be held constant within 2°C in the range of 20 to 30°C during colour development. The colour is read after 10 to 12 minutes at 690 nm using a suitable spectrophotometer. The absorbance is compared with a calibration curve, using a distilled water blank. In addition, a reagent blank must be run. The timing is critical because the colour develops progressively and later fades.

11.4 Qualitative Method for the Detection of Ammonium Phosphates in Water

The sample is collected as in Section 11.3.1. A 1 mL volume of sample is transferred to a beaker. A 5 mL volume of concentrated nitric acid is added and the solution evaporated down to approximately 1 mL. This should be done in a fume hood. A 2 mL volume of water is added and the solution transferred to a test tube. A 1 mL volume of 1 M ammonium nitrate and 2 mL of 0.5 M ammonium molybdate are added to the test tube. The contents are then heated to boiling. A yellow precipitate indicates the presence of phosphate (Welcher 1955).

11.5 Quantitative Method for the Detection of Ammonium Phosphates in Soil

11.5.1 Titrimetric (AOAC 1925). A 5 g soil sample and 10 g of sodium peroxide are mixed in a porcelain crucible. The mixture is heated with a bunsen burner until a reaction starts then the crucible is covered and low red heat is used for 30 minutes. The mixture is quantitatively transferred to a 500 mL volumetric flask using hot water for rinsing. The mixture is then acidified with concentrated hydrochloric acid and then boiled. The solution is cooled and made to volume with water. The silica is allowed to settle and a clear 200 mL aliquot of solution is removed.

Dilute (50 percent) ammonium hydroxide is added to precipitate iron, aluminum, and phosphorus, and the solution is filtered. The precipitate is washed with hot water several times and then placed in a beaker. Hot dilute (25 percent) hydrochloric acid is added to the beaker to dissolve the precipitate. The solution is evaporated to dryness on a water bath and the silica removed by filtration. The filtrate is evaporated to approximately 10 mL and 2 mL of concentrated nitric acid is added. The excess acid is neutralized with dilute (50 percent) ammonium hydroxide followed by the addition of concentrated nitric acid until the solution clears. The solution is heated to between 40 and 50°C on a water bath, then 15 mL of molybdate solution is added. The temperature is maintained for 1 to 2 hours. The solution is left to stand overnight, filtered, and the residue is washed free from the acid with cold water. The filter plus residue is transferred to a small beaker and dissolved in sodium or potassium hydroxide. The excess alkali is titrated with standardized nitric acid using phenolphthalein indicator (AOAC 1925).

11.6 Qualitative Method for the Detection of Ammonium Phosphates in Soil

The sample is prepared as in Section 11.5.1 up to the removal of a clear 200 mL aliquot. A 1 mL volume of sample is placed in a test tube and 4 mL of 6 M hydrochloric acid is added. The solution is heated to boiling and hydrogen sulphide is bubbled in. The solution is then centrifuged and the supernatant treated with 5 mL of concentrated nitric acid and evaporated to approximately 1 mL in a fume hood. A 2 mL volume of water is added followed by 1 mL of 1.0 M ammonium nitrate and 2 mL of 0.5 M ammonium molybdate. The solution is heated to boiling. A yellow precipitate indicates phosphates (Welcher 1955).

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EnviroTIPS

Common Abbreviations

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