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Problem

Spills

ZINC SULPHATE

TP
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1985

May 1985

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

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

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ZINC SULPHATE

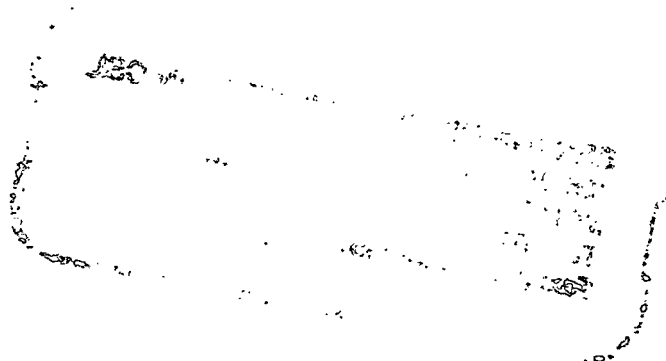
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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS



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

May 1985



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

ZINC SULPHATE (ZnSO_4)

Colourless to white crystals (anhydrous) or crystalline powder (hydrate) with no odour.

SYNONYMS

Zinc Sulphate Monohydrate, Zinc Sulphate Heptahydrate, Sulphuric Acid Zinc Salt, Sulfate de Zinc (Fr.), White Copperas, White Vitriol, Zinc Vitriol

TRADE NAMES

Bonazen, Bufopto Zinc Sulphate, Op-Thal-Zin, Zinkosite

IDENTIFICATION NUMBERS

UN No. NA 9161; CAS No. 7733-02-0; OHM-TADS No. 7216958; STCC No. 4963786

GRADES & PURITIES

Anhydrous: >99 percent zinc sulphate

Monohydrate: fertilizer grade, containing minimum 36 percent zinc

IMMEDIATE CONCERNS

Fire: Not combustible

Human Health: Moderately toxic

Environment: Harmful to aquatic life and plants in very low concentrations

PHYSICAL PROPERTY DATA

	<u>Anhydrous</u>	<u>Monohydrate</u>
State (15°C, 1 atm):	Solid	Solid
Melting Point:	Decomposes before melting (680°C)	(238°C)
Flammability:	Noncombustible	Noncombustible
Specific Gravity:	3.74 (20°C)	3.28 (20°C)
Solubility (in water):	53.8 g/100 g (20°C)	65 g/100 g (20°C)
Behaviour (in water):	Sinks and mixes, no reaction	
Odour Threshold:	Odourless	Odourless

ENVIRONMENTAL CONCERNS

Zinc is toxic to aquatic life at concentrations as low as 90 µg/L. It can accumulate in tissues and bones and is persistent in the environment.

HUMAN HEALTH

No TLV® or IDLH established

Exposure Effects

Inhalation (of dust): Irritation to the nose, throat, and respiratory and digestive systems.

Contact: Irritation to skin and eyes with possible dermatitis, boils and conjunctivitis.

Ingestion: Causes burning pain in throat and stomach, vomiting, diarrhea, hypotension, cold sweats, retching, possible collapse and convulsions, and possibly death.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Notify manufacturer and environmental authorities. Contain spill, if safe to do so. Avoid contact with solid and dust. Keep contaminated water from entering sewers or watercourses.

Fire Control

Most fire extinguishing agents may be used where zinc sulphate is involved.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Remove material by manual or mechanical means. Avoid dusting when picking up solid.

Water: Contain by damming, water diversion or natural barriers. Treat contaminated water.

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties	Anhydrous	Monohydrate
Appearance	White solid	White, free-flowing crystals (Virginia MSDS)
Usual shipping state	Solid	Solid
Physical state at 15°C, 1 atm	Solid	Solid
Melting point	Decomposes before melting (CRC 1980)	
Decomposition temperature	680°C (looses SO ₃ , forms 3ZnO•2SO ₃) 930°C (forms ZnO) (ACS 1972)	238°C (looses H ₂ O) (Virginia TD)
Densities		
Density	3.74 g/cm ³ (20°C) (Bailar 1973)	3.28 g/cm ³ (20°C) (Bailar 1973)
Specific gravity	3.54 (25°/4°C) (CRC 1980)	
	3.74 (Virginia TD)	3.28 (Virginia TD)
Bulk density		1400 kg/m ³ (packed) (Virginia TD)
Fire Properties		
Flammability	Noncombustible (CHRIS 1978)	Noncombustible (Virginia MSDS)
Other Properties		
Molecular weight of pure substance	161.43 (CRC 1980)	179.46 (Virginia TD; CRC 1980)
Constituent components of typical commercial grade	>99 percent ZnSO ₄	36 percent (min.) Zn, 20 ppm (max.) Pb, 20 ppm (max.) Fe, 100 ppm (max.) chlorides (Virginia TD)
Refractive index	1.669 (CRC 1980)	1.67 (Virginia TD)

	Anhydrous	Monohydrate
Viscosity	2.15 mPa·s (10 percent solution, 20°C) (CRC 1980)	
Heat of formation	-983.5 kJ/mole (25°C) (Virginia TD)	-1299.6 kJ/mole (25°C) (Virginia TD)
Entropy	124.7 J/mole (Virginia TD)	146.0 J/mole (Virginia TD)
Heat of solution	77.4 kJ/mole (18°C) (Perry 1973)	41.6 kJ/mole (20°C) (ACS 1972; Bailar 1973)
Heat capacity constant pressure (Cp)	117 J/(mole·°C) (25°C) (ACS 1972; Bailar 1973)	145 J/(mole·°C) (25°C) (Virginia TD)
pH of aqueous solution	-	5.4 (1.0 percent by wt. solution, 20°C) (Virginia TD)
Eutectic compositions	27.2 percent aqueous solution (f.p. -6.5°C) (Lange's Handbook 1979)	
Solubility		
In water	41.9 g/100 g (Kirk-Othmer 1984) 53.8 g/100 g (20°C) (Virginia TD)	65 g/100 g (20°C) (Virginia MSDS)
In other common materials	Soluble in methanol and glycerin (CRC 1980)	

Chemical and Physical Properties

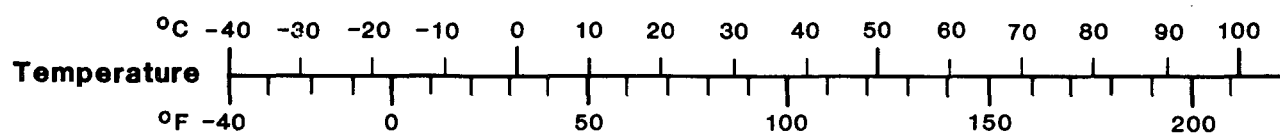
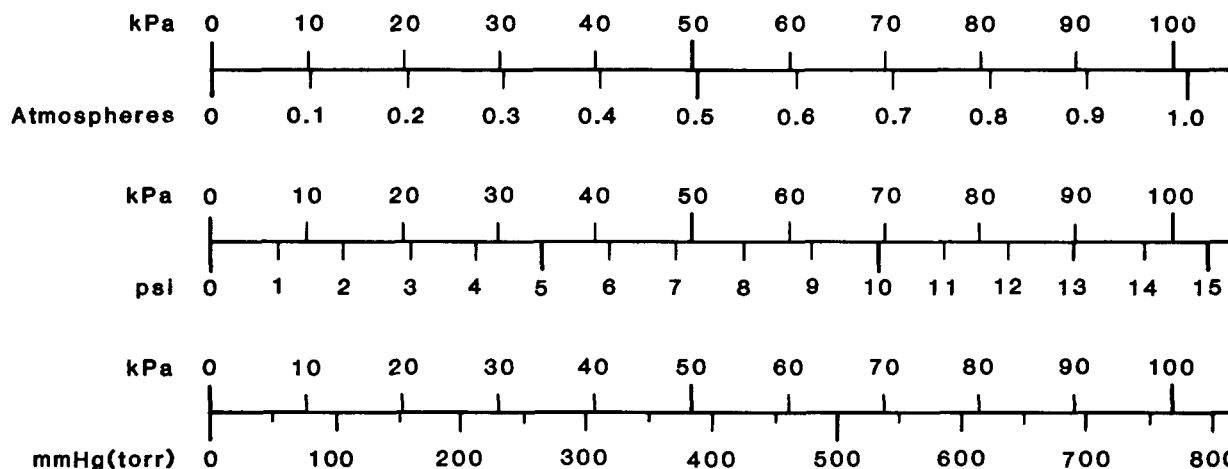
Zinc sulphate forms a number of hydrates, three of which are stable: $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ (monohydrate, stable at 60–100°C in solution), $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ (hexahydrate, stable at 39–60°C in solution), and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (heptahydrate, stable at 0–39°C in solution) (Kirk-Othmer 1984; Bailar 1973). Three unstable hydrates are also formed: $\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (monoclinic).

The properties of the anhydrous and monohydrate forms is given above. The heptahydrate (i.e., the stable form) is also available commercially and contains 54 percent ZnSO_4 equivalent. Its crystalline form consists of $\text{Zn}(\text{H}_2\text{O})_6$ octahedra and SO_4

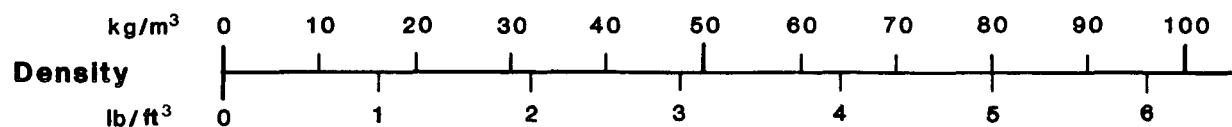
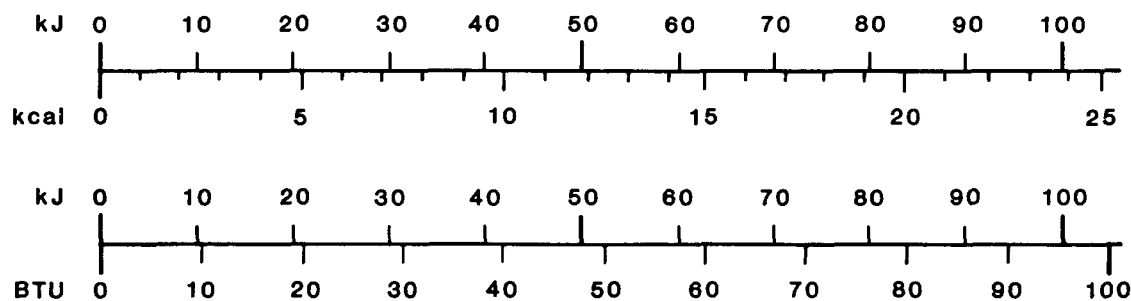
tetrahedra with a (H₂O) in the gap between these. It has a density of 1.966, loses water at 100°C and loses all its water of hydration at 280°C. The heat of solution is -17.8 kJ/mole at 20°C (Ullmann 1975; Bailar 1973).

ZINC SULPHATE

CONVERSION NOMOGRAMS

**Pressure** 1 kPa = 1 000 Pa**Viscosity**

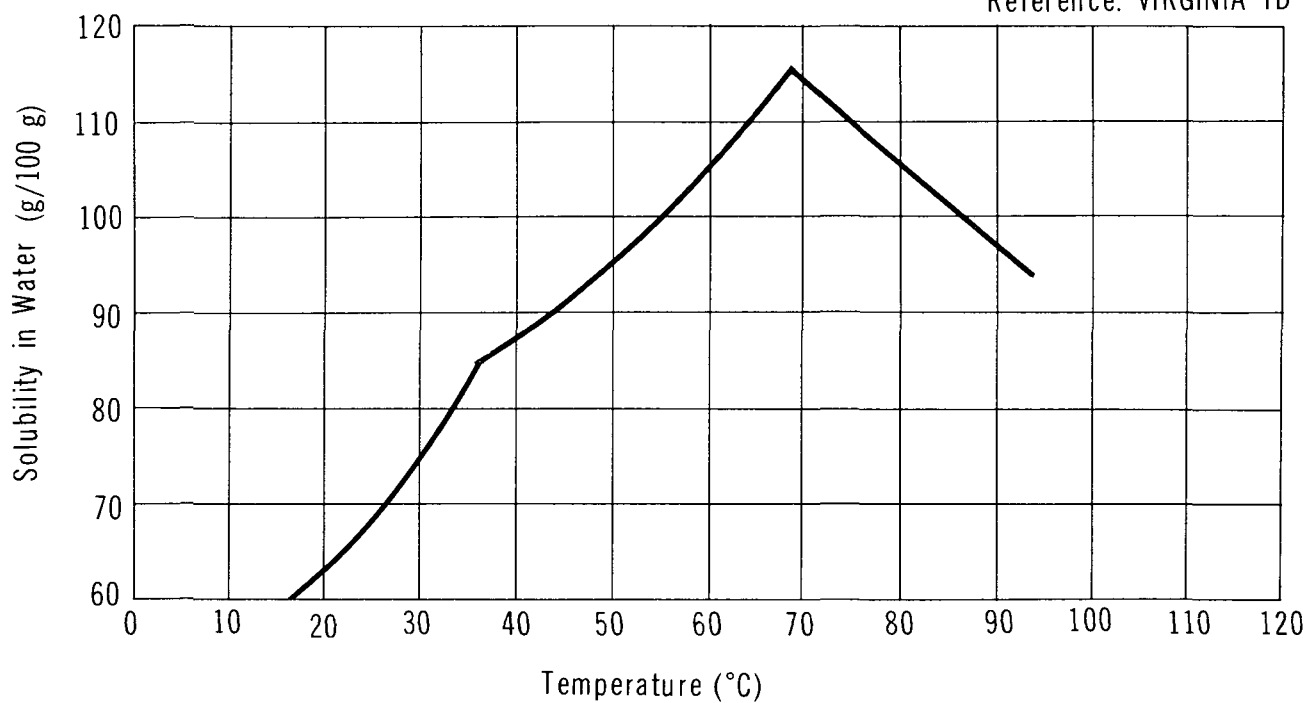
Dynamic 1 Pa·s = 1 000 centipoise (cP)

Kinematic 1 m²/s = 1 000 000 centistokes (cSt)**Concentration (in water)**1 ppm \cong 1 mg/L**Energy (heat)** 1 kJ = 1 000 J

ZINC SULPHATE

SOLUBILITY IN WATER vs TEMPERATURE

Reference: VIRGINIA TD



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Corpus 1980; Virginia Bul. 802; Virginia Bul. 807B)

Zinc sulphate is most commonly sold as the monohydrate containing a minimum of 36 percent zinc. The pure anhydrous form with a purity in excess of 91 percent and the heptahydrate are also occasionally sold.

3.2 Domestic Manufacturers (CBG 1980; CCPA 1981; Corpus 1980)

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

Anachemia Ltd.
P.O. Box 147
Lachine, Quebec
H8S 4A7
(514) 489-5711

Hudson Bay Mining and Smelting Co. Ltd.
P.O. Box 28, Toronto Dominion Centre
Toronto, Ontario
M5K 1B8
(416) 362-2192

Canadian Electrolytic Zinc Ltd.
860 boul. Cadieux
Valleyfield, Quebec
J6S 4W2
(514) 373-9144

Texasgulf Canada
Commerce Court West, Suite 5000
P.O. Box 175, Commerce Court
Toronto, Ontario
M3C 2S2
(416) 869-1200

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

3.3 Other Suppliers (CBG 1980; Corpus 1980)

Aldert Chemicals Ltd.
648 Finch Avenue East
Willowdale, Ontario
M2K 2E6
(416) 223-0404

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

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

Degussa (Canada) Ltd.
3370 South Service Road
Burlington, Ontario
L7N 3M6
(416) 639-5710

Harrison and Crosfield (Canada) Ltd. 4 Banigan Drive Toronto, Ontario M4H 1G1 (416) 425-6500	Phillip Brothers (Canada) Ltd. 1245 Sherbrooke Street West Montreal, Quebec H3G 1G9 (514) 845-4294
International Chemical Canada Ltd. P.O. Box 385 Brampton, Ontario L6V 2L3 (416) 453-4234	Pigment and Chemical Co. Ltd., The 5757 Cavendish Blvd. Montreal, Quebec H4W 2W8 (514) 489-9396
Kingsley and Keith (Canada) Ltd. 310 Victoria Avenue Montreal, Quebec H3Z 2M8 (514) 487-1550	Quadra Chemicals Ltd. 7575 TransCanada Highway St. Laurent, Quebec H4T 1V6 (514) 337-2454
MacKenzie and Feimann Ltd. 970 Malkin Avenue Vancouver 4, British Columbia (604) 253-6335	Van Waters and Rogers Ltd. 9800 Van Horne Way Richmond, British Columbia V6X 1W5 (604) 273-1441

3.4 Major Transportation Routes

Current Canadian production of zinc sulphate occurs in four provinces: British Columbia produces 39 percent of total production, Quebec produces 32 percent, Ontario produces 7 percent, and Manitoba produces 12 percent. Where not used captively, zinc sulphate is shipped in bags or drums by rail or truck.

3.5 Production Levels (Corpus 1980)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1979)
Canadian Electrolytic Zinc, Valleyfield, Que. (captive)	506
Cominco, Trail, B.C. (captive)	604.5
Hudson Bay Mining and Smelting, Flin Flon, Man. (captive)	184
Texasgulf of Canada, Timmins, Ont. (captive)	269
TOTAL	1563.5
Domestic Production (1979)	1320
Imports (1979)	1.9
TOTAL SUPPLY	1321.9

3.6 **Manufacture of Zinc Sulphate**

Zinc sulphate is produced by the reaction of zinc oxide and sulphuric acid.

3.6.1 Manufacturing Process. Crude zinc oxide is mixed with aqueous sulphuric acid in a leach tank to produce a zinc sulphate solution:



The solution is filtered to remove insoluble impurities, then treated with zinc dust to precipitate metallic contaminants. In Canada, most zinc sulphate solution is used in the production of zinc (captive). If zinc sulphate is to be produced, the solution is evaporated to dryness at low temperatures, producing the monohydrate, $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ (EPA 530/SW-104c).

3.7 **Major Uses in Canada (Corpus 1980)**

Zinc sulphate is used in the following processes: zinc refining, mineral depressant, rayon precipitant and agricultural fertilizer.

3.8 **Major Buyers in Canada (Corpus 1980)**

Asarco, Grand Falls, Nfld.
 Brunswick Mining, Bathurst, N.B.
 Canada Packers, Toronto, Ont.
 Courtaulds Canada, Cornwall, Ont.
 Heath Steele, Newcastle, N.B.
 Hudson Bay Mining & Smelting, Flin Flon, Man.
 Mattabi Mines, Sturgeon Lake, Ont.
 Noranda Mines, Manitouwadge, Ont.
 Texasgulf Canada, Timmins, Ont.
 Western Mines, Campbell R., B.C.
 Willroy Mines, Manitouwadge, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 General. Zinc sulphate is shipped bulk in railway box cars, covered hopper cars and covered hopper trucks. Occasionally, zinc sulphate solutions are transported by rail in a tank car such as class 111A60W1. Current transport regulations do not specifically apply to this commodity (RTDCR 1974).

Most small quantities of zinc sulphate are transported in bags. Multi-wall moisture-proof bags of 23 kg (50 lb.) and 45 kg (100 lb.) are most common.

4.1.2 Packaging. In addition to bulk shipments, zinc sulphate solid is also transported in drums and boxes. Drums fabricated from a variety of construction materials are permitted. Table 2 listing drum types and descriptions is included (TDGC 1980). The following packaging systems are also used (TDGC 1980):

- Wooden box with inside container fabricated of glass, metal, plastic or earthenware. 10 L capacity each container.
- Fibreboard box with inside receptacle as above. 5 L capacity each receptacle.
- Metal box with total capacity of not more than 40 L.

TABLE 2 DRUMS

Type of Drum	Designation	Description	Figure No. (If Any)
Steel	1A1	Nonremovable head, reusable	2
	1A1A	1A1 with reinforced chime	2
	1A1B	1A1 with welded closure flange	2
	1A1C	1A1 with lead coating	2
	1A1D	1A1 with coating (other than lead)	2
	1A2	Removable head, reusable	2
	1A2A	1A2 with reinforced chime	2
	1A2B	1A2 with lead coating	2
	1A3	Nonremovable head, single use only	2
	1A4	Removable head, single use only	2
Monel*	TC5M		2
Aluminum	1B1	Nonremovable head	2
	1B2	Removable head	2

TABLE 2 DRUMS (Cont'd)

Type of Drum	Designation	Description	Figure No. (If Any)
Plywood	1D2		
Fibreboard	1G1	Convolutely wound plies. Maximum capacity 250 L (55 gal.). Maximum net mass 400 kg (882 lb.)	
Plastic	1H1	Nonremovable head. Maximum capacity 250 L (55 gal.). Maximum net mass 400 kg (882 lb.)	
	1H2	Same as 1H1 except head removable	
Steel drum with inner plastic receptacle	6HA1	Outer sheet in the shape of drum. Inner plastic receptacle. Maximum capacity 225 L (49 gal.)	
Plywood drum with inner plastic receptacle	6HD1	Outer plywood in shape of drum. Inner plastic receptacle. Maximum capacity 225 L (49 gal.)	
Fibreboard drum inner plastic receptacle	6HG1	Outer container of convolutely wound plies of fibreboard. Inner plastic in shape of drum. Maximum capacity 225 L (49 gal.)	

* See Section 4.3 of this Report.

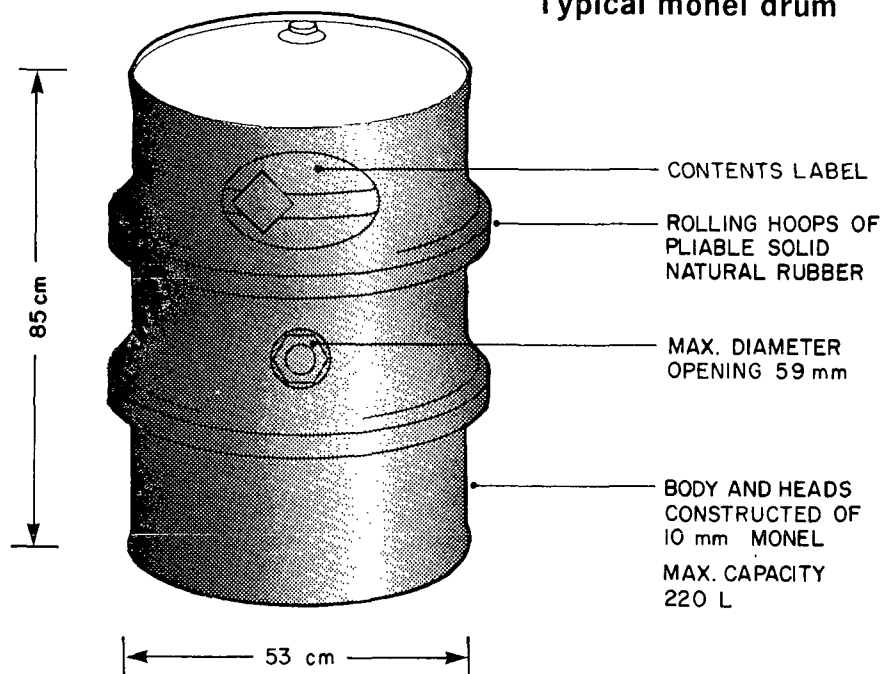
4.2 Specifications and Materials for Off-loading Equipment

The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in zinc sulphate solution service. It is recognized that other materials may be used for particular applications, as indicated in Table 3. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets, pumps

ZINC SULPHATE

TYPICAL DRUM CONTAINERS

Typical monel drum



Typical steel drum

MIN. 2.4 mm
LEAD COATING FOR
IAC DESIGNATION

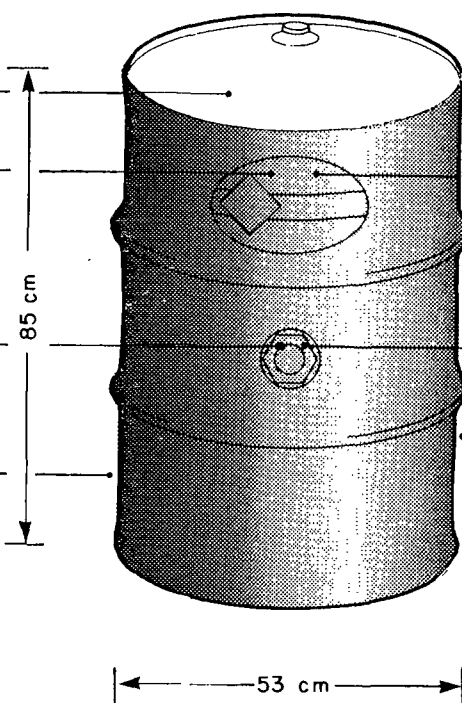
CONTENTS LABEL

MAX. DIAMETER
OPENING 70 mm

BODY AND HEADS
CONSTRUCTED OF
ROLLED STEEL

MAX. CAPACITY
250 L

MAX. NET MASS
400 kg



Typical aluminum drum

CONTENTS LABEL

MAX. DIAMETER
OPENING 70 mm

BODY AND HEADS
CONSTRUCTED OF
MIN. 99% PURE
ALUMINUM

MAX. CAPACITY
250 L

MAX. NET MASS
400 kg

and storage tanks. For off-loading zinc sulphate bulk solids, chutes and hoppers, etc., can be made of ordinary steel plate. Normal solids handling equipment is used.

Schedule 40 stainless steel pipes and fittings are recommended for solutions at room temperature. Above this temperature, pipes and fittings should be lined with polypropylene or chlorinated polyether resin (DCRG 1978). The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on tank cars, but process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines should be self-draining. Flexible steel hose or solid pipe with swivel joints may be used for the flexible sections of the unloading line. Either the ball bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance. Some installations of flexible line are made with standard fittings using a number of threaded elbows.

Cast iron or cast steel diaphragm valves with polypropylene resin liner will serve adequately for all concentrations at almost all temperatures (DCRG 1978). Polypropylene can be used as a gasket material (DCRG 1978).

A single-suction centrifugal pump with stainless steel shaft and a cast stainless steel casing and impeller is recommended for pumping (HIS 1969). The material selected, however, must be chosen with concentration and temperature in mind. Back vanes on the impeller, an extra long stuffing box with a flowing water seal, and polypropylene packing will help reduce leakage. The pump and motor should be directly connected but not close-coupled. Welded carbon steel storage tanks with a rubber lining or stainless steel cladding are commonly used. At elevated temperatures, a Hypalon liner inside the tank is recommended (GF).

4.3 Compatibility with Materials of Construction

The compatibility of zinc sulphate with materials of construction is indicated in Table 3. The unbracketed abbreviations are described in Table 4. The rating system for this report is briefly described below:

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

TABLE 3 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	Most Solutions	24	PVDC (DCRG 1978)		
		49	PE (DPPED 1967)		
		60	PVC I PVC II (DPPED 1967)		
		71	ABS (DPPED 1967)		
		93	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	30%	Hot and Cold	SS 316 (JSSV 1979)		
3. Pumps	Aqueous Solution		All Bronze SS 316 (HIS 1969)		
4. Others	Saturated	20	SS 316 (ASS)	SS 302 SS 304 SS 430 (ASS)	
		60	uPVC, PE PP, NR NBR, IIR EPDM, CR FPM, CSM (GF)	POM (GF)	

TABLE 3 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
4. Others (cont'd)		80	PP, NBR IIR, EPDM CR, FPM CSM (GF)	PE (GF)	uPVC, NR POM (GF)
		60	PVC (TPS 1978)		
		82	PP (TPS 1978)		
		85	CPVC (TPS 1978)		
		121	PVDF (TPS 1978) SBR (GPP)		
	10-30%	24-100	Glass (CDS 1967)		
	10%	24			Concrete (CDS 1967)
	30%	24			Concrete (CDS 1967)
	10-20, 100%	24	Wood (CDS 1967)		
	Diluted	60	uPVC, PE PP, NR NBR, IIR EPDM, CR FPM, CSM (GF)	POM (GF)	
	5, 25%	20	SS 302 SS 304 SS 316 (ASS)	SS 430 (ASS)	SS 410 (ASS)
	25%	Boiling	SS 316 (ASS)	SS 302 SS 304 (ASS)	SS 410 SS 430 (ASS)

TABLE 4 MATERIALS OF CONSTRUCTION

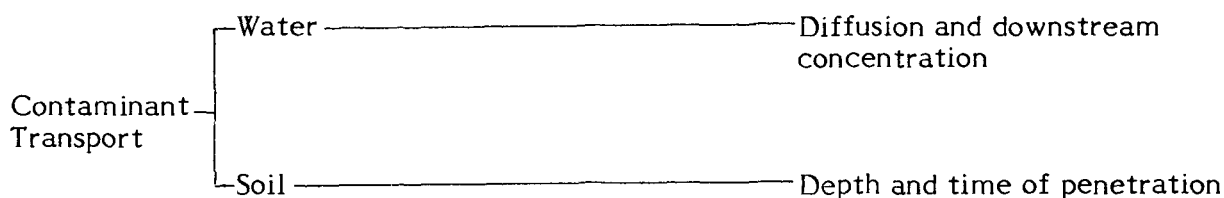
Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene Aluminum Bronze Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene) Rubber
CSM	Chlorosulphonated Polyethylene (Hypalon) Earthenware
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton) Glass
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber Nickel 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 N) Rubber
SS (followed by grade)	Stainless Steel
uPVC	Unplasticized Polyvinyl Chloride Wood (Spruce)

5 CONTAMINANT TRANSPORT

5.1 General Summary

Zinc sulphate is commonly transported as a solid, primarily in bags and drums, and occasionally bulk in hopper type or pneumatic bulk railway cars. Zinc sulphate will dissolve rapidly in water and penetrate into the soil at a rate dependent on the soil type and its water content. Transport of zinc sulphate toward the water table may be an environmental problem.

Because zinc sulphate is essentially nonvolatile, dispersion in air is not a problem. Zinc sulphate as a dust may present a problem in certain spill situations. Factors to be considered for the transport of a zinc sulphate spill in water and soil are as follows:



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

Since zinc sulphate is primarily transported as a solid, no leak nomograms have been prepared.

5.3 Dispersion in the Air

Because zinc sulphate 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, zinc sulphate 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 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 zinc sulphate is denser than water, the maximum concentration would be expected to be 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 4: time versus distance for a range of average stream velocities
- Figure 5: hydraulic radius versus channel width for a range of stream depths
- Figure 6: diffusion coefficient versus hydraulic radius for a range of average stream velocities
- Figure 7: α^* versus diffusion coefficient for various time intervals
- Figure 8: α versus δ^* for a range of spill sizes
- Figure 9: maximum concentration versus δ for a range of river cross-sectional areas

Lakes or Still Water Bodies

- Figure 10: volume versus radius for the hazard zone for a range of lake depths
- Figure 11: average concentration versus volume for the hazard zone for a range of spill sizes

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

The flowchart in Figure 3 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 4 through 11) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 4: Time versus distance. Figure 4 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 4.

Figure 5: 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 longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 5 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 6: Diffusion coefficient versus hydraulic radius. Figure 6 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 5 and the average stream velocity (U).

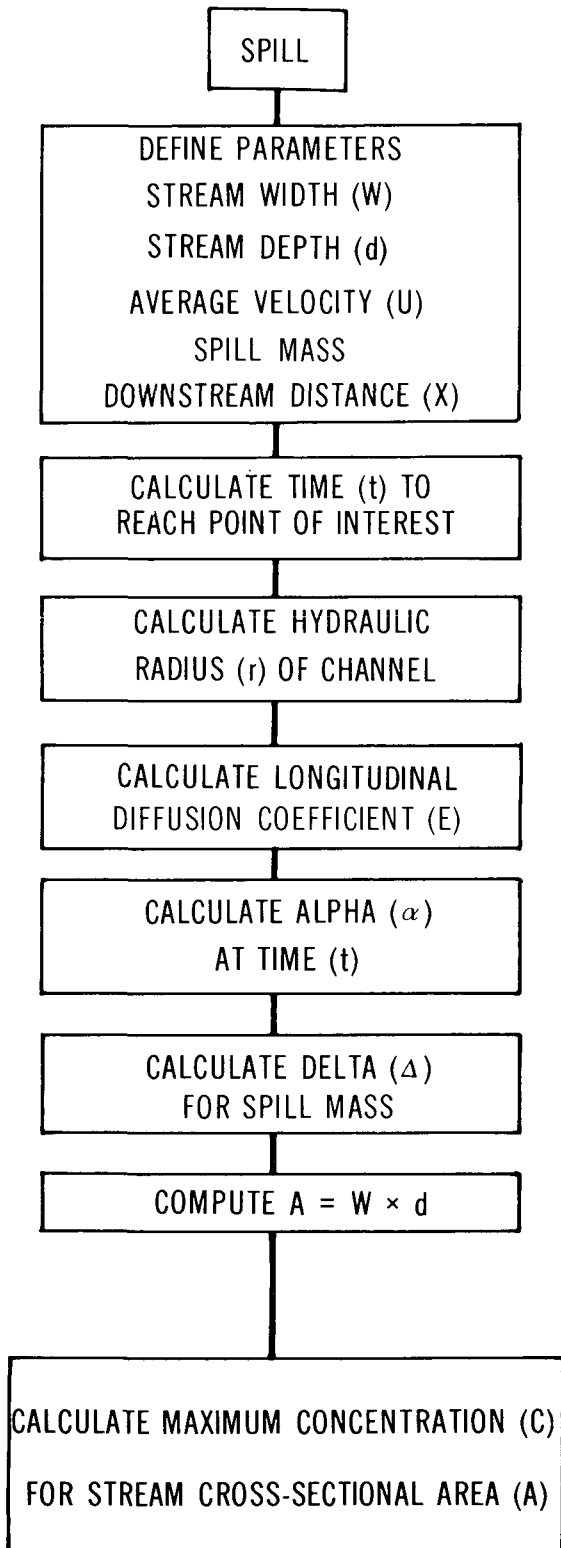
Figure 7: Alpha versus diffusion coefficient. Figure 7 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 8: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 8 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 9: Maximum concentration versus delta. Figure 9 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-section area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 9 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

ZINC SULPHATE

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 4

t = _____ minutes

Step 3: Use Figure 5

r = _____ m

Step 4: Use Figure 6

E = _____ m²/s

Step 5: Use Figure 7

α = _____

Step 6: Use Figure 8

Δ = _____

Step 7: Compute stream cross-sectional

Area (A)

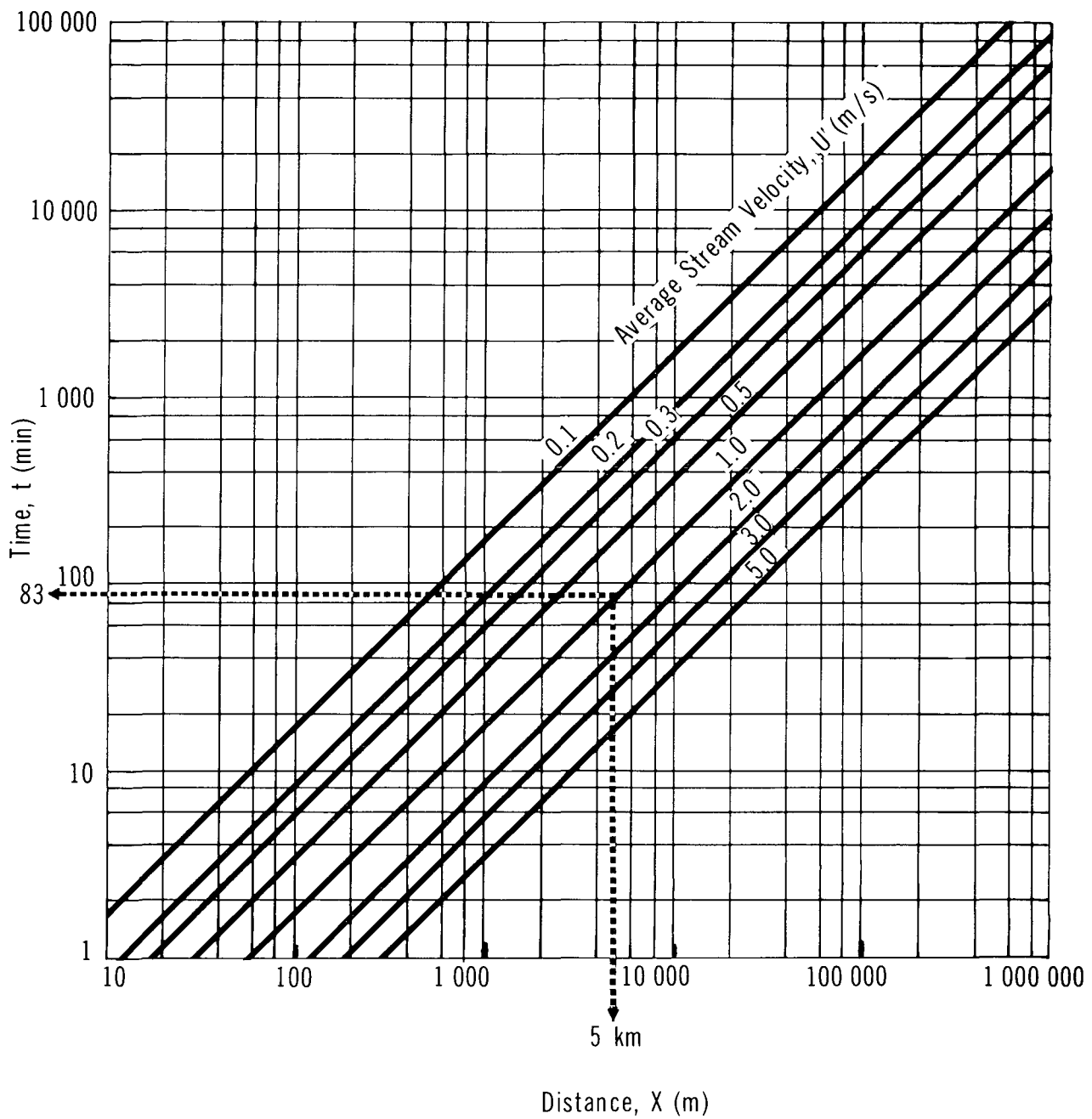
A = W × d _____ m²

Step 8: Use Figure 9

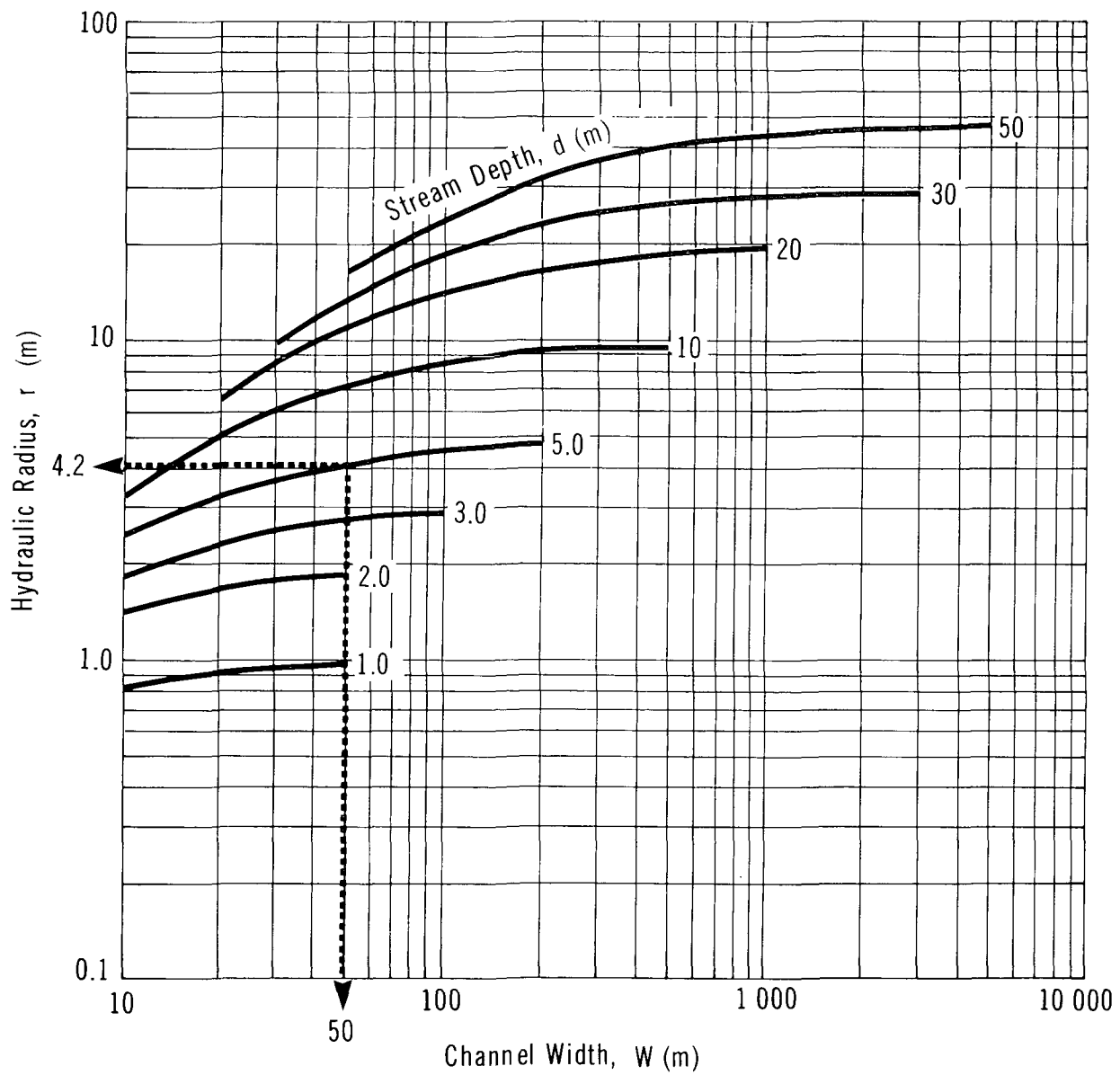
C = _____ ppm

ZINC SULPHATE

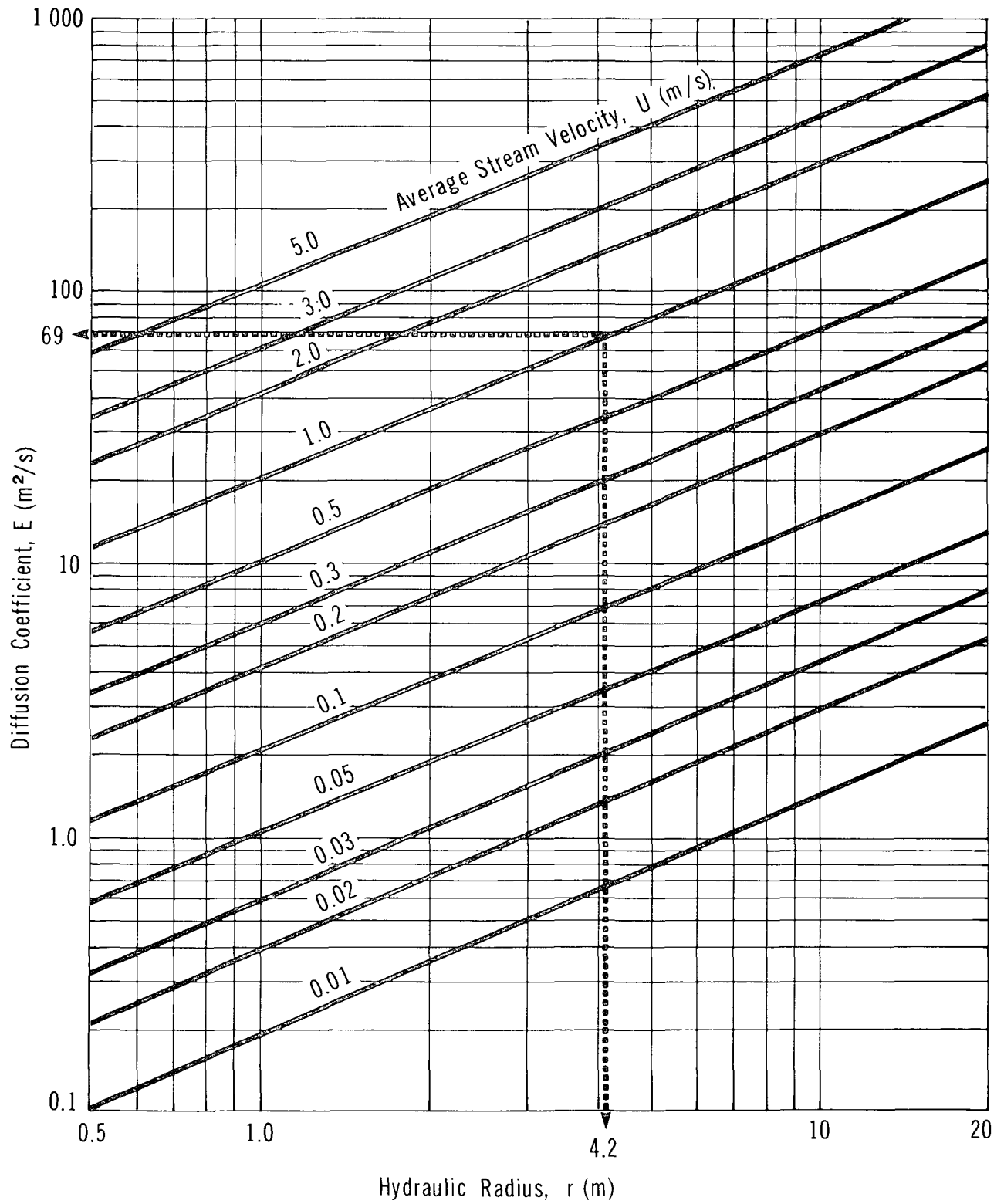
TIME vs DISTANCE



ZINC SULPHATE

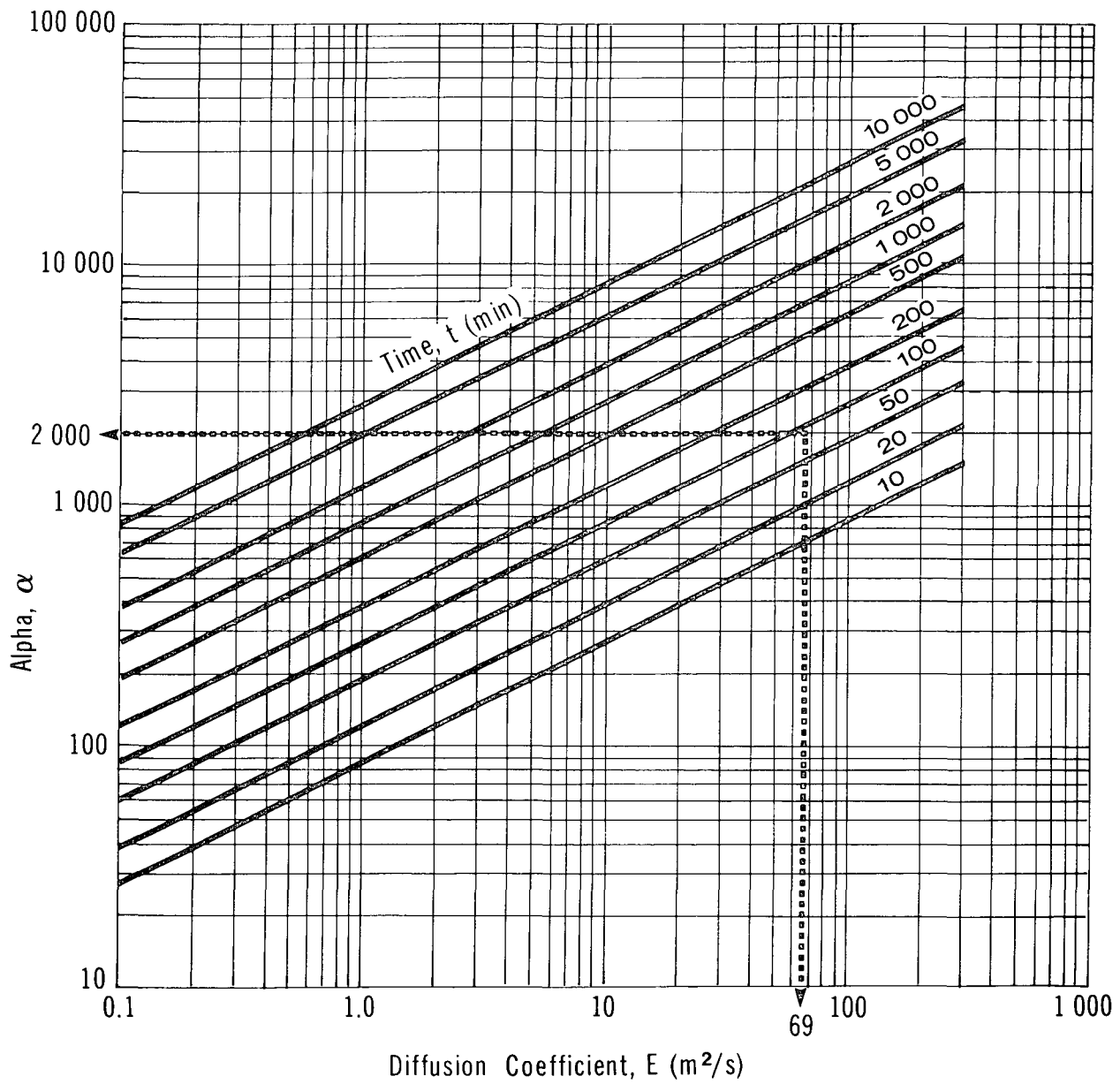
HYDRAULIC RADIUS VS
CHANNEL WIDTH

ZINC SULPHATE

DIFFUSION COEFFICIENT
VS HYDRAULIC RADIUS

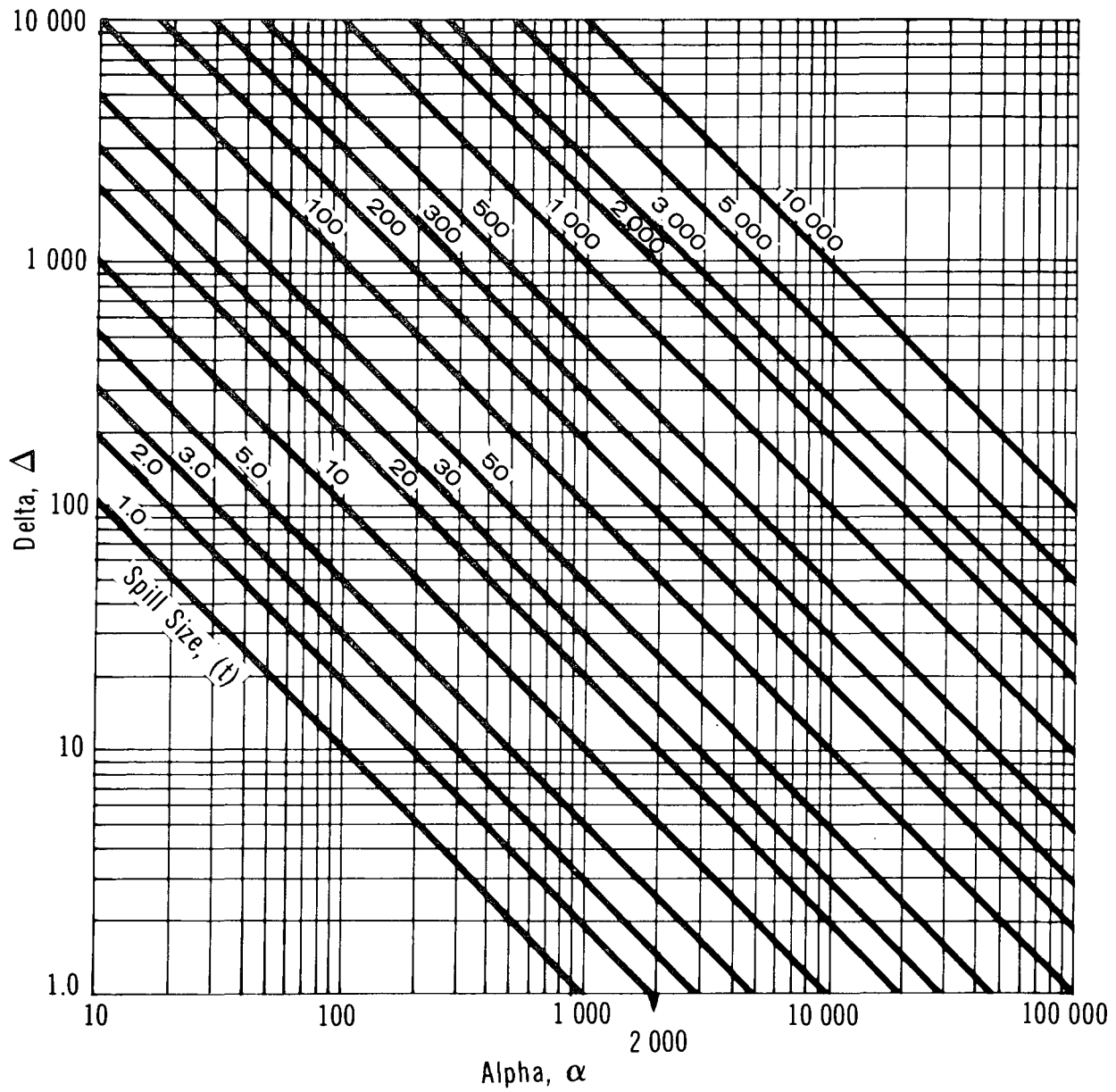
ZINC SULPHATE

ALPHA vs DIFFUSION COEFFICIENT



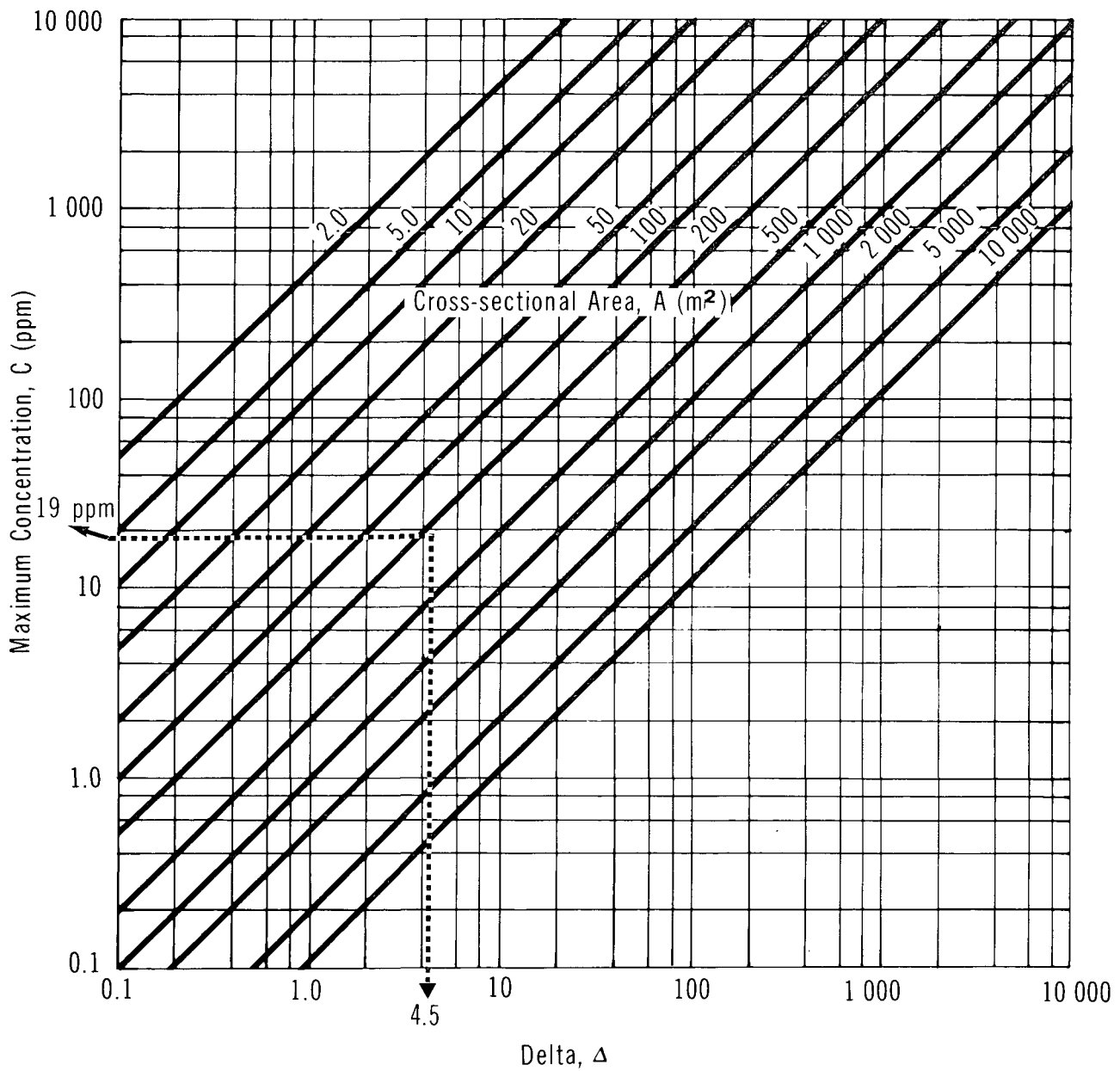
ZINC SULPHATE

ALPHA vs DELTA



ZINC SULPHATE

MAXIMUM CONCENTRATION vs DELTA



5.4.2.2 Nomograms for lakes or still water bodies.

Figure 10: 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 10. The radius (r) represents the distance from the spill to the point of interest.

Figure 11: 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 11 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 20 tonne spill of 45 percent zinc sulphate solution has occurred in a river. The stream width is 50 m and stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

- $W = 50 \text{ m}$
- $d = 5 \text{ m}$
- $U = 1 \text{ m/s}$
- spill size = 20 tonnes of 45 percent zinc sulphate solution, contains the equivalent of 9 tonnes of zinc sulphate

Step 2: Calculate the time to reach the point of interest

- Use Figure 4
- With $X = 5000 \text{ m}$ and $U = 1 \text{ m/s}$, $t = 83 \text{ min}$

Step 3: Calculate the hydraulic radius (r)

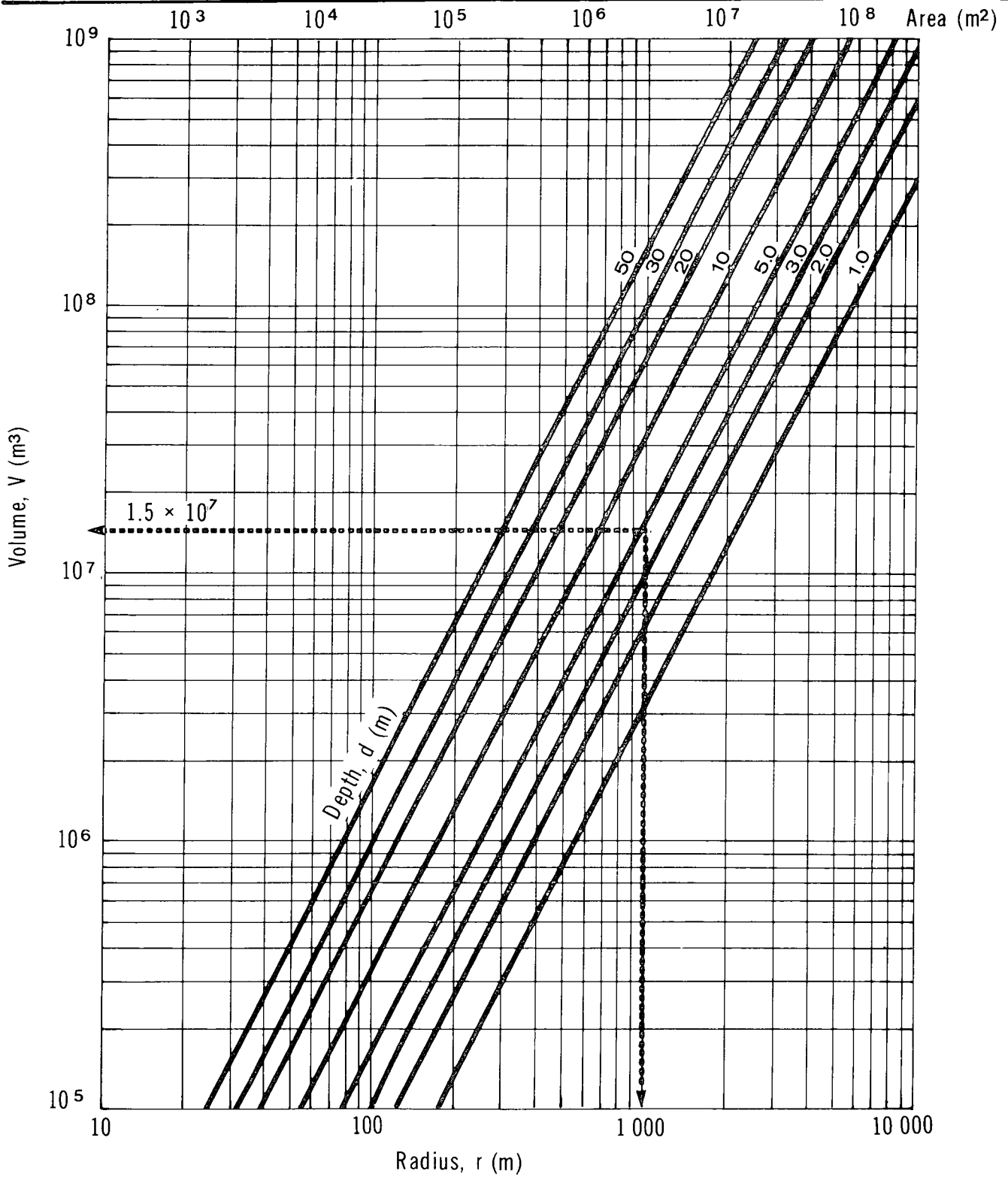
- Use Figure 5
- With $W = 50 \text{ m}$ and $d = 5 \text{ m}$, $r = 4.2 \text{ m}$

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 6
- With $r = 4.2 \text{ m}$ and $U = 1 \text{ m/s}$, $E = 69 \text{ m}^2/\text{s}$

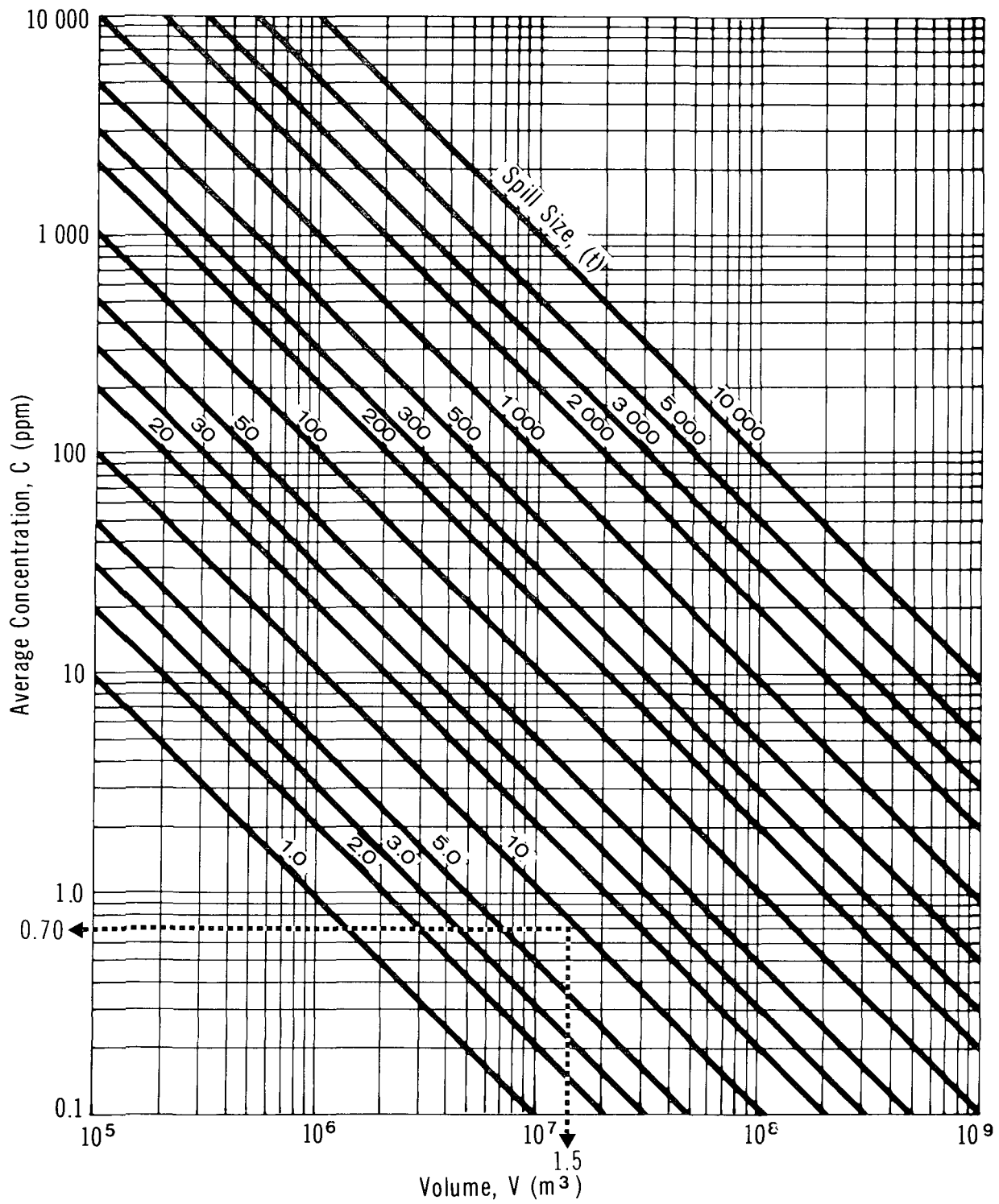
ZINC SULPHATE

VOLUME vs RADIUS



ZINC SULPHATE

AVERAGE CONCENTRATION vs VOLUME



- Step 5: Calculate alpha (α)
- Use Figure 7
 - With $E = 69 \text{ m}^2/\text{s}$ and $t = 83 \text{ min}$, $\alpha = 2000$
- Step 6: Calculate delta (Δ)
- Use Figure 8
 - With alpha (α) = 2000 and spill size = 9 tonnes (zinc sulphate), delta (Δ) = 4.5
- 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 9
 - With $\Delta = 4.5$ and $A = 250 \text{ m}^2$, $C = 19 \text{ ppm}$

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 9 tonne spill of zinc sulphate 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
- $d = 5 \text{ m}$
 - $r = 1000 \text{ m}$
 - spill size = 9 tonnes
- Step 2: Determine the volume of water available for dilution
- Use Figure 10
 - With $r = 1000 \text{ m}$, $d = 5 \text{ m}$, the volume is approximately $1.5 \times 10^7 \text{ m}^3$
- Step 3: Determine the average concentration
- Use Figure 11
 - With $V = 1.5 \times 10^7 \text{ m}^3$ and spill size = 9 tonnes, the average concentration is 0.7 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Introduction. Zinc sulphate is conveyed primarily as a solid. Consequently, when spilled, only a limited groundwater contamination hazard exists if the soil is dry and if no precipitation falls prior to cleanup. However, if precipitation or other forms of moisture are present, groundwater contamination can be expected. Since zinc sulphate is

very soluble in water, concentrated solutions can infiltrate the soil. Some interaction between zinc sulphate and the soil will occur. However, much of the zinc sulphate 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 contaminant dissolved in the precipitation will run off. 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 concentration somewhat. This is shown schematically in Figure 12.

5.5.2 Equations Describing Dissolved Zinc Sulphate 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 Dissolved Zinc Sulphate in Soil. The saturated hydraulic conductivity (K_0), in m/s, is given by:

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

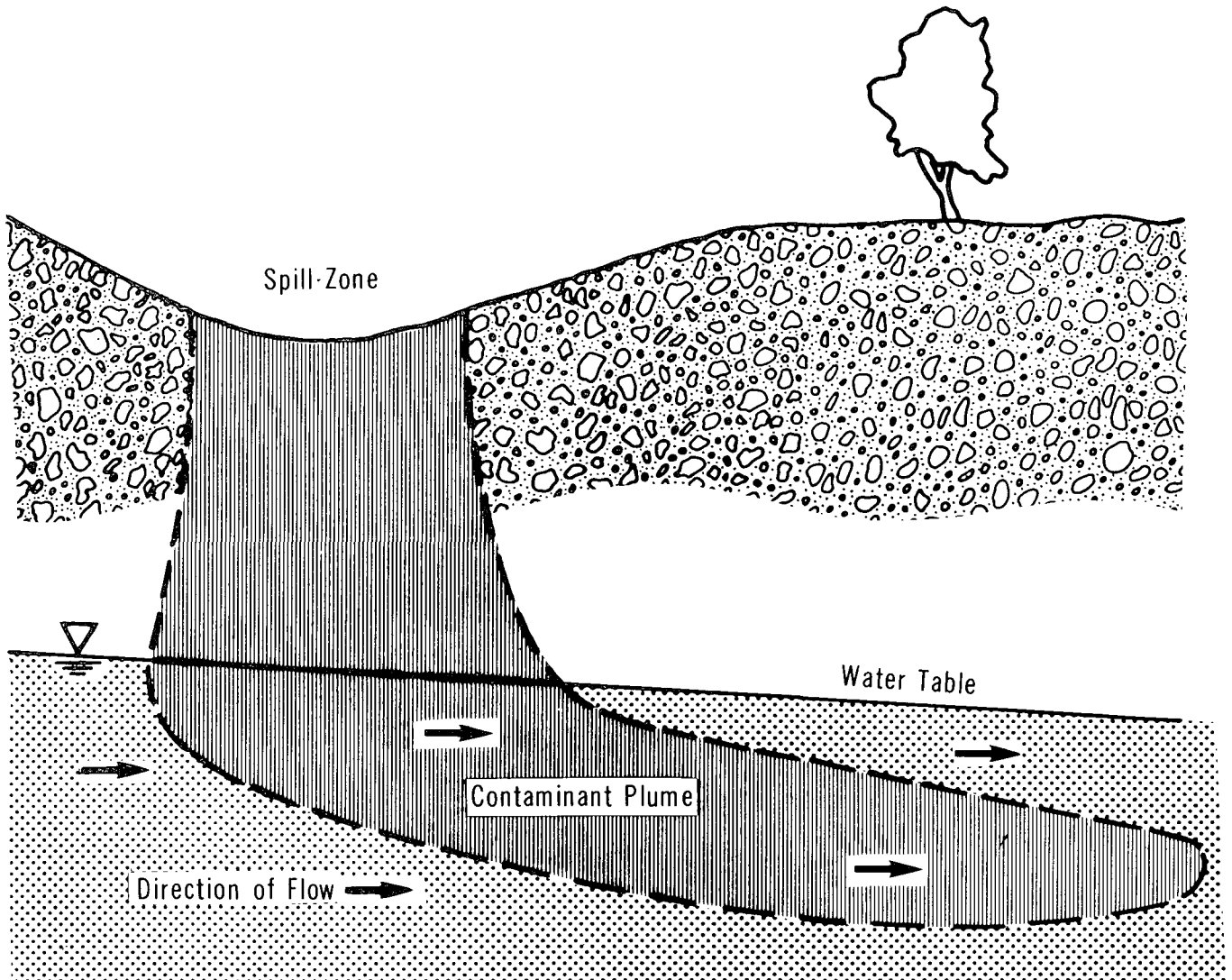
where: k = intrinsic permeability of the soil (m^2)
 ρ = mass density of the fluid (kg/m^3)
 μ = absolute viscosity of the fluid ($Pa \cdot s$)
 g = acceleration due to gravity = 9.81 m/s^2

Because of the manner in which the solution is created, i.e., precipitation falling on spilled solid, it is assumed to have fluid properties similar to those of water.

Property	Dilute Solution (4°C)	Water (20°C)
Mass density (ρ), kg/m^3	1000	998
Absolute viscosity (μ), $Pa \cdot s$	1.57×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_0), m/s	$(0.62 \times 10^7)k$	$(0.98 \times 10^7)k$

ZINC SULPHATE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

5.5.4 Soils. Three soils are selected for this work. Their relevant properties are:

Property	Soil Type		
	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 dissolved zinc sulphate 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 13. The nomograms are presented as Figures 14, 15 and 16.

5.5.6 Sample Calculation. A 20 tonne spill of zinc sulphate has occurred on silty sand soil. The radius of the spill is 8.6 m and the temperature is 20°C. Rain begins prior to cleanup. Calculate the depth of contaminant penetration 4 days after commencement of the rainfall.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- $T = 20^\circ\text{C}$
- $r = 8.6\text{ m}$
- Soil = silty sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 4 days

Step 2: Calculate the area of spill

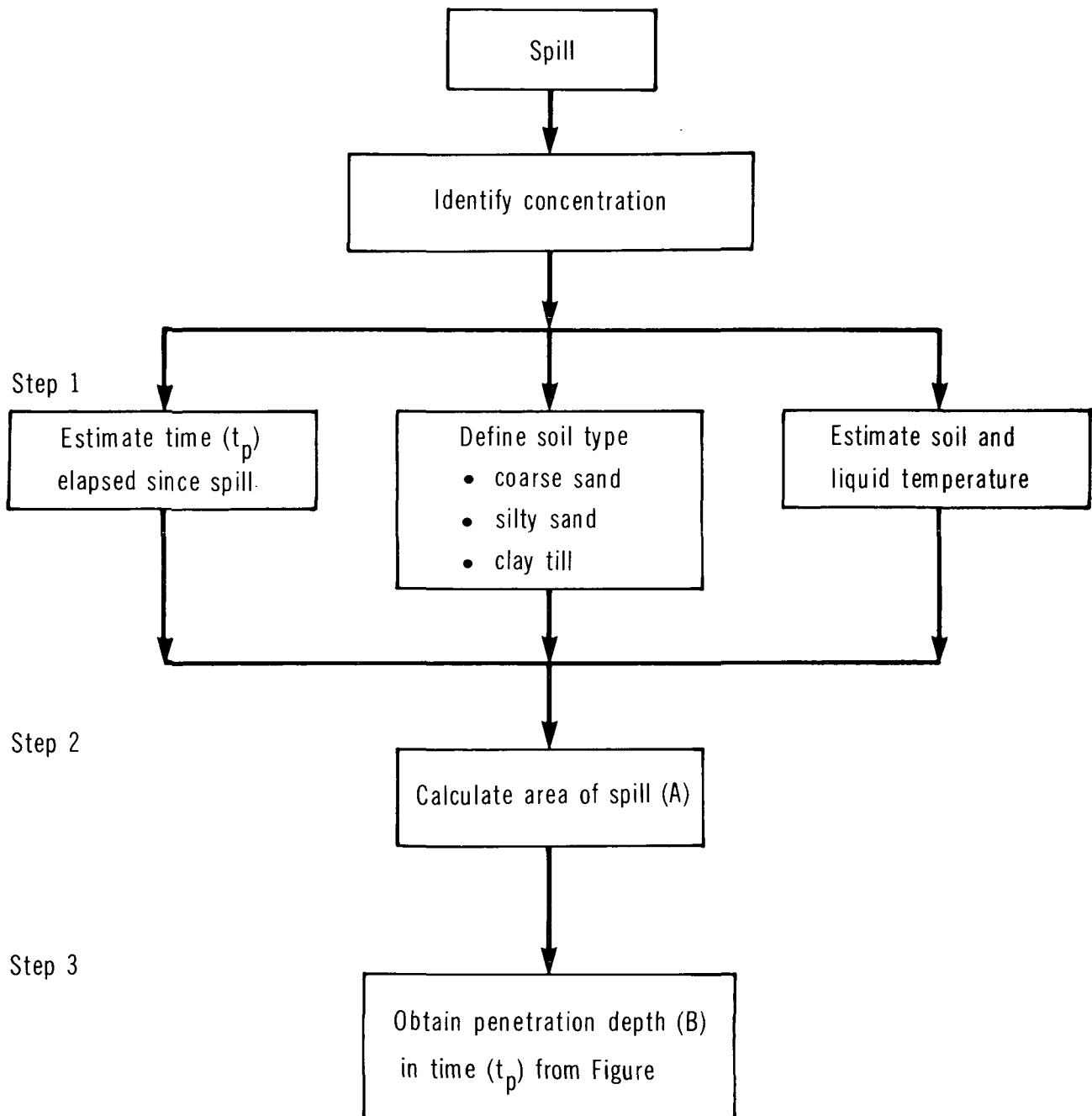
- $A = \pi r^2 = 232\text{ m}^2$

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

- For silty sand, and $t_p = 4$ days, the penetration is 3.4 m

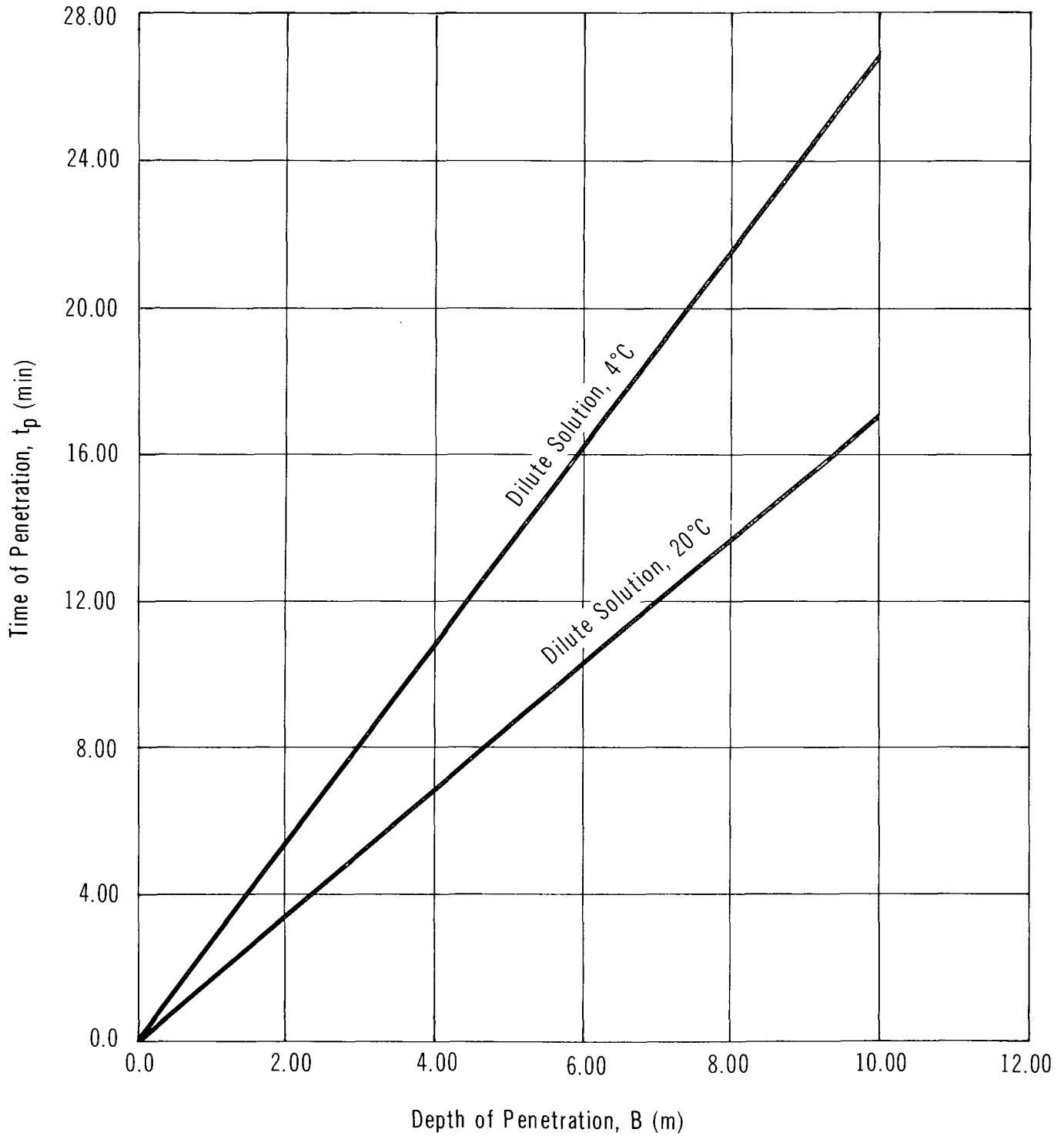
ZINC SULPHATE

FLOWCHART FOR NOMOGRAM USE

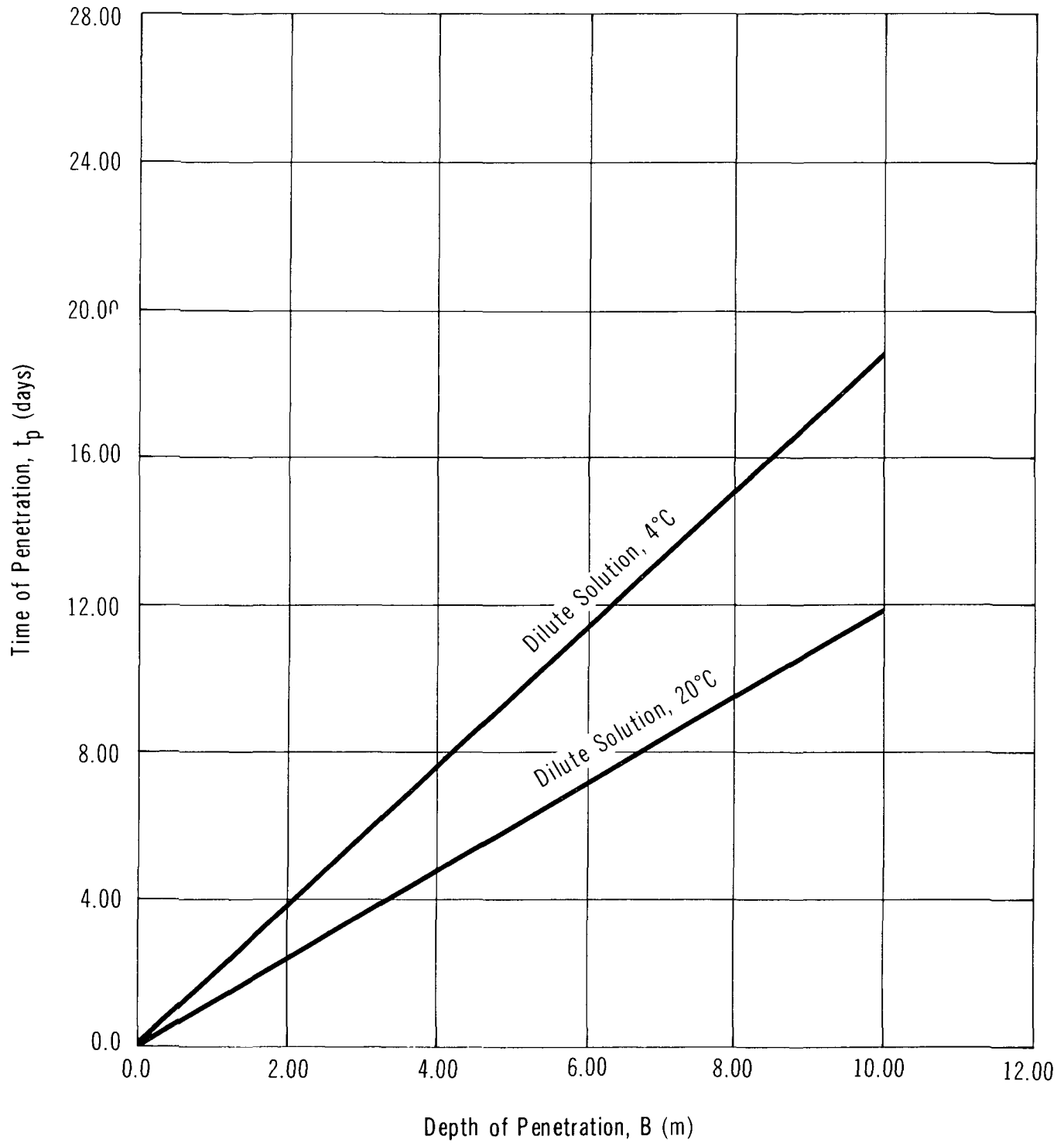


ZINC SULPHATE

PENETRATION IN COARSE SAND

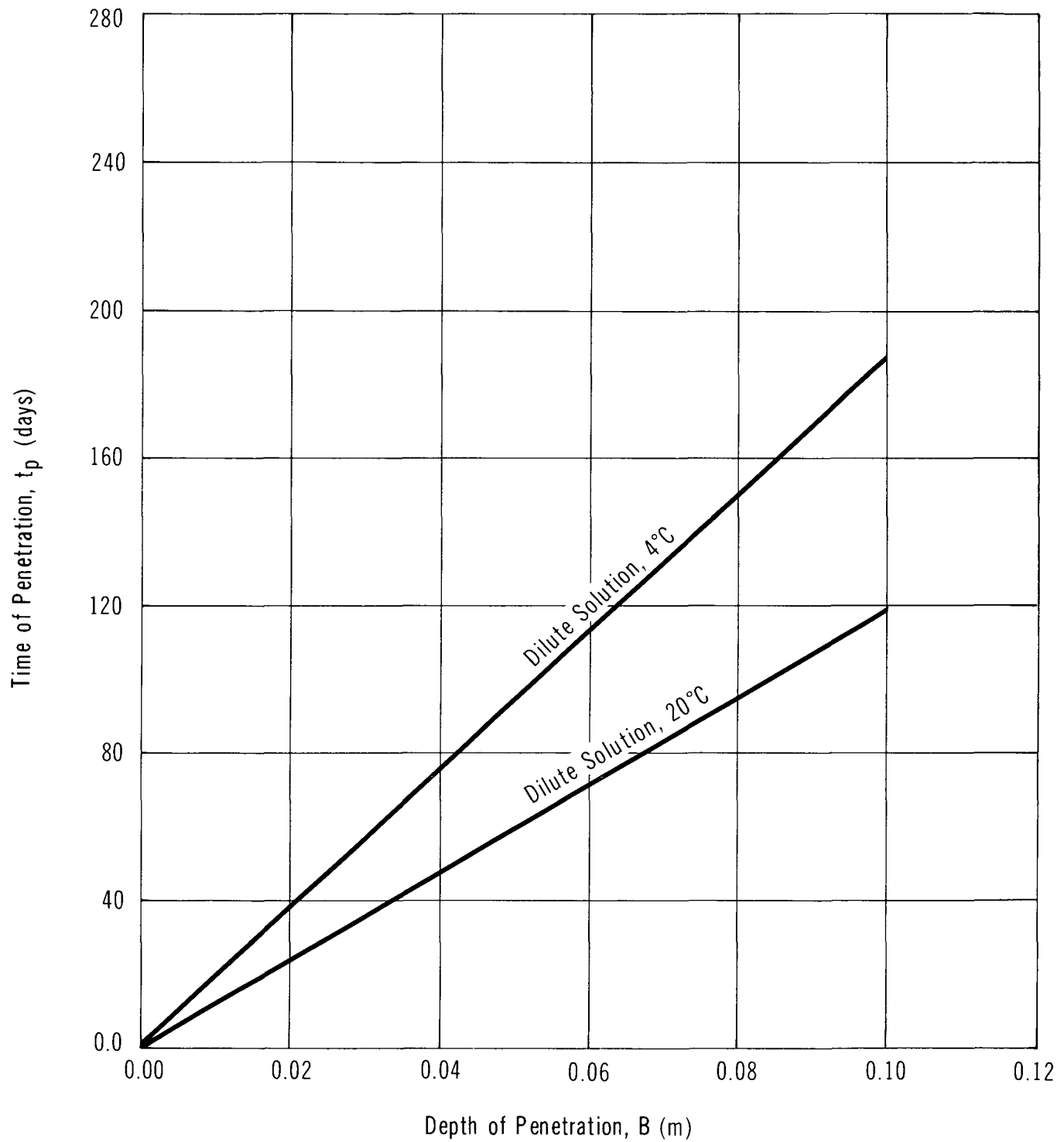


ZINC SULPHATE

PENETRATION IN SILTY SAND

ZINC SULPHATE

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water.

6.1.1.1 Canada. The recommended limit for sulphate in drinking water is 500 mg/L and the objective concentration is <150 mg/L. The limit for zinc in drinking water is 5.0 mg/L (Guidelines/Canadian/Waters 1978). In Ontario, the recommended limit for sulphate in drinking water is 250 mg/L (Water Management Goals 1978).

The recommended maximum concentrations of zinc in irrigation waters used continuously on all soils is 2.0 mg/L. For use up to 20 years on fine textured soils of pH 6.0 to 8.5, 10 mg/L is acceptable (Water Management Goals 1978). The recommended zinc upper limit for livestock watering is 25 mg/L (WQC 1972).

The above recommendations have been reviewed and the following are the current recommended objectives (Taylor 1980):

Uses	Recommended objectives (as total zinc)
Raw public water supply	5 mg/L 10 mg/L for waters with predistribution treatment
Aquatic life and wildlife	0.05 mg/L, hardness 0-120 mg/L as CaCO ₃ 0.10 mg/L, hardness 120-180 mg/L as CaCO ₃ 0.20 mg/L, hardness 180-300 mg/L as CaCO ₃ 0.30 mg/L, hardness >300 mg/L as CaCO ₃
Agricultural water supply	
Livestock watering	50 mg/L
Irrigation	1 mg/L in soils with pH <6.5 5 mg/L in soils with pH >6.5
Recreation and aesthetics	5 mg/L
Industrial water supplies	
Food processing	5 mg/L 10 mg/L for waters with predistribution treatment

6.1.1.2 Other countries. The permissible zinc concentration in surface water for public water supplies in the U.S. is 5.0 mg/L (WQCDB-2 1971). The standard for sulphate is 250 mg/L (Jorgensen 1979). The ambient water quality for the protection of aquatic life is 180 µg/L (HD = 50 mg CaCO₃), 320 µg/L (HD = 100) and 570 µg/L (HD = 200) (AWQC 1980).

The permissible limit for zinc in surface water for public supplies in the USSR is 1.0 mg/L (WQCDB-2 1971).

The European WHO standard (including France, Bulgaria and Sweden) for sulphate is 250 mg/L. The limit for zinc is 5.0 mg/L (WQCDB-2 1971; Jorgensen 1979).

6.1.2 Air. In Canada, the limit for zinc in free and combined form (half-hour average) is 100 g/m³ (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 Canada. The concentration of zinc in an unfiltered sample should not exceed 30 µg/L to protect aquatic life (Water Management Goals 1978).

6.2.2 Other Countries. The chronic aquatic toxicity limit for fish in the U.S. is 0.04 ppm (as zinc) (Pickering 1971). The limit for aquatic plants is 25 ppm (WQC 1973). Concentrations of zinc exceeding 0.1 mg/L constitute a hazard in the marine environment; levels less than 0.02 mg/L present minimal risk of deleterious effects (WQC 1972).

6.2.3 Measured Toxicities. All concentrations are expressed as mg/L zinc equivalent rather than ZnSO₄ equivalent, except where noted. To convert these to ZnSO₄ mg/L, multiply by 2.47.

6.2.3.1 Freshwater toxicity.

Zn Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Fish Kill Data</u>					
20	24	Zebra fish	lethal		WQCBD-5 1973
40	-	Rainbow trout	changes in gill tissue, death		Skidmore 1972

Zn Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.7	108	Threespine stickleback	lethal		WQCDB-3 1971
6	48	Rainbow trout fingerlings	lethal		Wilber 1969
1000	1 to 4	Goldfish	lethal	hard water	Ellis 1967
16	20	Young eels	lethal		WQC 1963
<u>Fish Toxicity Tests</u>					
10.0 to 12.6	120	<i>Abramis brana</i>	LC ₅₀	10-13°C, HD=290 pH=7.2-7.9	Nriagu 1980
0.34 to 1.6	504	Atlantic salmon (juveniles)	LC ₅₀	HD=12-24, 10°C, flow-through	AWQC 1980; JWPCF 1980
8.8 to 19.1	24	Bluegill (<i>Lepomis macrochirus</i>)	LC ₅₀	HD=40	AWQC 1980
4	48	Bluegill	LC ₅₀	-	WQC 1972
2.35	96	Bluegill	LC ₅₀	HD=45	AWQC 1980
4.8 to 5.8	96	Bluegill	LC ₅₀	static, HD=20	AWQC 1980
9.9 to 12.1	96	Bluegill	LC ₅₀	flow-through, HD=20	AWQC 1980
11.0	336	Bluegill	LC ₅₀	-	JWPCF 1983
7.2 to 12.0	480	Bluegill	LC ₅₀	HD=370	AWQC 1980
1.8	15, 20	Brook trout (<i>Salvelinus fontinalis</i>), 3-8 g, 8-15 g	LC ₅₀	flow-through, 15°C	Sprague 1968
1.0	42, 54	Brook trout, 3-8 g, 8-15 g	LC ₅₀	flow-through, 15°C	Sprague 1968
0.32	47	Brook trout, 4 g	LC ₅₀	flow-through, 15°C	Sprague 1968
1.0	71.5	Brook trout, 3.2 g	LC ₅₀	flow-through, 15°C	Sprague 1968

Zn Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
2.0	96	Brook trout	LC ₅₀	HD=45.4 pH=7.0-7.7	Holcombe 1979
1.5 to 2.1	96	Brook trout	LC ₅₀	flow- through, HD=47	AWQC 1980
6.1 to 7.0	96	Brook trout	LC ₅₀	flow- through, HD=178, 179	AWQC 1980
0.64	336	Brook trout (juveniles)	LC ₅₀	soft	McKim 1975
31	48	Channel catfish (<i>Ictalurus punctatus</i>)	LC ₅₀	-	JWPCF 1983
30	96	Channel catfish	LC ₅₀	-	JWPCF 1983
8.2	336	Channel catfish	LC ₅₀	-	JWPCF 1983
0.09	96	Cut-throat trout (<i>Salmo clarki</i>)	LC ₅₀	reaerated	AWQC 1980
0.96	96	Fathead minnow (<i>Pimephales promelas</i>)	LC ₅₀	soft water	Pickering 1971
2.6 to 10	96	Fathead minnow	LC ₅₀	flow- through, HD=200	AWQC 1980
12 to 13	96	Fathead minnow	LC ₅₀	static, HD=200	AWQC 1980
12.5 to 13.8	96	Fathead minnow	LC ₅₀	flow- through, HD=50	AWQC 1980
18.5 to 25	96	Fathead minnow	LC ₅₀	flow- through, HD=100	AWQC 1980
29 to 35.5	96	Fathead minnow	LC ₅₀	flow- through, HD=200	AWQC 1980
1.5	96	Flagfish, juveniles (<i>Jordanella floridae</i>)	LC ₅₀	25°C, HD=44, pH=7.1-7.8	Spehar 1976
7.7 to 11.4	24	Golden shiner	LC ₅₀	HD=40	AWQC 1980
24 to 103	24	Goldfish	LC ₅₀	HD=40	AWQC 1980

Zn Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
7.5	96	Goldfish	LC ₅₀	HD=45	AWQC 1980
6.15	48	Guppy (<i>Poecilla reticulata</i>)	LC ₅₀	static	JWPCF 1981
1.3 to 30	96	Guppy	LC ₅₀	static, HD=20, 45	AWQC 1980
1.5	96	Guppy, juveniles	LC ₅₀	flow- through, 25°C, HD=30, pH=7.2	JWPCF 1982
1.7	96	Guppy, juveniles	LC ₅₀	static, 25°C, HD=30, pH=7.2	JWPCF 1982
5.1 to 6.4	96	Guppy	LC ₅₀	static, 25°C	JWPCF 1982
8.0	336	Largemouth bass	LC ₅₀	static, 25°C	JWPCF 1983
2.5	120	<i>Noemacheilus barbatulus</i>	LC ₅₀	HD=240-290, pH=7.2-7.8	Nriagu 1980
16.0	120	Perch (<i>Perca fluviatilis</i>)	LC ₅₀	HD=290, 10.4-13.8°C	Nriagu 1980
33.3	96	<i>Puntius conchoni</i>	LC ₅₀	static, HD=310, 13-19°C	JWPCF 1981
1.24	24	Rainbow trout (<i>Salmo gairdnerii</i>)	LC ₅₀	HD=40	AWQC 1980
1.24	24	Rainbow trout	LC ₅₀	flow- through, HD=5.0, 20-25°C	JWPCF 1977
2.4 to 5.0	48	Rainbow trout	LC ₅₀	HD=320	AWQC 1980
4.0	48	Rainbow trout	LC ₅₀	HD=240-290, pH=7.5-7.9	Nriagu 1980
0.5	64	Rainbow trout	LC ₅₀	-	Jones 1969
0.24 to 0.83	96	Rainbow trout	LC ₅₀	flow- through, HD=30	AWQC 1980
2.5 to 2.96	96	Rainbow trout	LC ₅₀	flow- through, HD=178	AWQC 1980

Zn Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
7.2	96	Rainbow trout	LC ₅₀	flow- through, HD=333	AWQC 1980
4.6	120	Rainbow trout	LC ₅₀	HD=290, 14.5-15.8°C, pH=7.3-7.9	Nriagu 1980
0.56	168	Rainbow trout	LC ₅₀	HD=15.2	AWQC 1980
0.5 to 1.0	504	Rainbow trout	LC ₅₀	HD=14	AWQC 1980
1.12	672	Rainbow trout	LC ₅₀	-	JWPCF 1983
1.12	2040	Rainbow trout	growth reduction	flow- through, HD=374	JWPCF 1978
17.3	120	Roach (<i>Rutilus rutilus</i>)	LC ₅₀	HD=290, 10-13°C, pH=7.2-7.9	Nriagu 1980
1.1	96	Sockeye salmon	LC ₅₀	soft, 12°C	Chapman
0.3	204	Stickleback	LC ₅₀	-	Jones 1969
11.2	24	Striped bass	LC ₅₀	Hudson River	Rehwoldo
10.0	48	Striped bass	LC ₅₀	Hudson River	Rehwoldo
6.7	96	Striped bass	LC ₅₀	Hudson River	Rehwoldo
<u>Insects (water-inhabiting)</u>					
180	96	Argia	LC ₅₀	HD=20, 20°C	Nriagu 1980
32	264	Caddisfly	lethal	-	WQCDB-5 1973
16	240	Mayfly (<i>Ephemerella grandis</i>)	lethal	-	WQCDB-5 1973
>9.2	336	Mayfly	LC ₅₀	HD=30-70	AWQC 1980
0.3	72	Mayfly nymphs	minimum tolerance	Idaho Lake water	WQC 1963
32.6	96	Sowbug	LC ₅₀	HD=100	AWQC 1978
32	240	Stonefly (<i>Acroneuria lycorias</i>)	LC ₅₀	HD=30-70	AWQC 1980
36.8	48	<i>Tanytarsus dissimilis</i>	LC ₅₀	static	JWPCF 1980

Zn Conc. (mg/L)	Time (hours)	Species	Result	Test Conditions	Reference
<u>Freshwater Plants</u> (larger species)					
67.7	672	Duckweed (<i>Lemna minor</i>)	EC ₅₀		AWQC 1980
22.5	672	<i>Elodea canadensis</i>	LC ₅₀		AWQC 1980
8.1	672	<i>Elodea canadensis</i>	EC ₅₀		AWQC 1980
<u>Microorganisms</u>					
15	168	Algae (<i>Chlamydomonas</i> sp.)	EC ₅₀	-	AWQC 1980
20	336	Algae (<i>Scenedesmus quadricauda</i>)	EC ₅₀	-	AWQC 1980
1.0 to 1.4	48 to 96	Algae, green	median threshold	-	WQC 1963
1.4 to 2.3	48 to 96	Bacteria (<i>E. coli</i>)	median threshold	-	WQC 1963
2.62	96	Protozoa (<i>Tetrahymena pyriformis</i>)	LC ₅₀	23-25°C	Nriagu 1980
6.67	96	Protozoa (unspecified)	LC ₅₀	distilled water	Carter 1973
1.2	24	Rotifer (<i>Philodina acuticornis</i>)	LC ₅₀	softwater, 20°C	Nriagu 1980
0.9	48	Rotifer (<i>Philodina acuticornis</i>)	LC ₅₀	softwater, 20°C	Nriagu 1980
0.902	48	Rotifer (unspecified)	LC ₅₀	HD=81	AWQC 1978
<u>Invertebrates</u>					
100	48	Brown shrimp	LC ₅₀	15°C, dark	Portman 1970
0.5	48	Copepod (<i>Eudiaptomus padanus</i>)	LC ₅₀	10°C, sub- alpine lake water	Nriagu 1980
5.5	48	Copepod (<i>Cyclops abyssorum</i>)	LC ₅₀	10°C, sub- alpine lake water	Nriagu 1980
0.182	48	Copepod (unspecified)	LC ₅₀	HD=23	AWQC 1978
0.033	48	<i>Daphnia hyalina</i>	LC ₅₀	HD=23	AWQC 1978

Zn Conc. (mg/L)	Time (hours)	Species	Result	Test Conditions	Reference
0.04	48	<i>Daphnia hyalina</i>	LC ₅₀	subalpine lake water, 25°C, HD=31	Nriagu 1980
19	16	<i>Daphnia magna</i>	LC ₅₀		Nriagu 1980
5.3	24	<i>Daphnia magna</i>	LC ₅₀	20.5°C, HD=50	Berglind 1984
3.0	24	<i>Daphnia magna</i>	LC ₅₀	20.5°C, HD=250	Berglind 1984
14.9	24	<i>Daphnia magna</i>	LC ₅₀	25°C, HD=31	Nriagu 1980
0.56 to 2.3	48	<i>Daphnia magna</i>	LC ₅₀	HD=45	AWQC 1980
1.1	48	<i>Daphnia magna</i>	LC ₅₀	HD=50	Berglind 1984
1.7	48	<i>Daphnia magna</i>	LC ₅₀	HD=25	Berglind 1984
10.8	48	<i>Daphnia magna</i>	LC ₅₀	20-22°C, HD=5.8	Nriagu 1980
8.1	72	<i>Daphnia magna</i>	LC ₅₀	20-22°C, HD=5.8	Nriagu 1980
7.4	96	<i>Daphnia magna</i>	LC ₅₀	20-22°C, HD=5.8	Nriagu 1980
0.28 to 1.6	48	<i>Daphnia pulex</i>	LC ₅₀	HD=44	AWQC 1980
0.5	96	<i>Daphnia pulex</i>	LC ₅₀	HD=45	AWQC 1980
14.5	24	Decapod (<i>Paratya tasmaniensis</i>)	LC ₅₀	15°C, HD=10	Nriagu 1980
8.3	48	Decapod (<i>Paratya tasmaniensis</i>)	LC ₅₀	15°C, HD=10	Nriagu 1980
3.3	72	Decapod (<i>Paratya tasmaniensis</i>)	LC ₅₀	15°C, HD=10	Nriagu 1980
1.1	96	Decapod (<i>Paratya tasmaniensis</i>)	LC ₅₀	15°C, HD=10	Nriagu 1980
38.5	96	Isopod (<i>Asellus communis</i>)	LC ₅₀	20°C, HD=100	Nriagu 1980
56	96	Isopod (<i>Asellus communis</i>)	LC ₅₀	20°C, HD=20	Nriagu 1980
2.71	24	Mollusc (<i>Physa heterastroph</i>)	LC ₅₀	21°C, HD=20	Nriagu 1980

Zn Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
6.1	48	Mollusc (<i>Physa heterastropa</i>)	LC ₅₀	21°C, HD=20	Nriagu 1980
4.9	72, 96	Mollusc (<i>Physa heterastropa</i>)	LC ₅₀	21°C, HD=20	Nriagu 1980
4.07	24	Mollusc (<i>Physa heterastropa</i>)	LC ₅₀	21°C, HD=100	Nriagu 1980
3.62	48	Mollusc (<i>Physa heterastropa</i>)	LC ₅₀	21°C, HD=100	Nriagu 1980
3.10	72, 96	Mollusc (<i>Physa heterastropa</i>)	LC ₅₀	21°C, HD=100	Nriagu 1980
0.434	24, 48	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	11°C, HD=20	Nriagu 1980
0.303	72, 96	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	11°C, HD=20	Nriagu 1980
0.949	24	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	11°C, HD=100	Nriagu 1980
0.434	48, 72, 96	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	11°C, HD=100	Nriagu 1980
0.667	24	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	20°C, HD=20	Nriagu 1980
0.536	48	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	20°C, HD=20	Nriagu 1980
0.434	72, 96	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	20°C, HD=20	Nriagu 1980
3.5	24	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	20°C, HD=100	Nriagu 1980
2.76	48	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	20°C, HD=100	Nriagu 1980
1.96	72	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	20°C, HD=100	Nriagu 1980

Zn Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
1.7	96	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	20°C, HD=100	Nriagu 1980
0.598	24, 48	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	32°C, HD=20	Nriagu 1980
0.35	72, 96	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	32°C, HD=20	Nriagu 1980
1.28	24	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	32°C, HD=100	Nriagu 1980
1.11	48, 72, 96	Mollusc (<i>Physa heterastropa</i>), young adults	LC ₅₀	32°C, HD=100	Nriagu 1980
18.0	24	Mollusc (<i>Physa integra</i>)	LC ₅₀	24°C	Nriagu 1980
13.5	48	Mollusc (<i>Goniobasis livescens</i>)	LC ₅₀	aerated lake water	Nriagu 1980
4.4	24	Mollusc (<i>Lymnea emarginata</i>)	LC ₅₀	aerated lake water	Nriagu 1980
4.15	48	Mollusc (<i>Lymnea emarginata</i>)	LC ₅₀	aerated lake water	Nriagu 1980
11.07	24	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	12.8°C, HD=20	Nriagu 1980
8.7	48	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	12.8°C, HD=20	Nriagu 1980
0.96	72	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	12.8°C, HD=20	Nriagu 1980
0.87	96	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	12.8°C, HD=20	Nriagu 1980
11.07	24, 48	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	12.8°C, HD=100	Nriagu 1980
3.03	72, 96	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	12.8°C, HD=100	Nriagu 1980
12.66	24	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	23°C, HD=20	Nriagu 1980
1.88	48	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	23°C, HD=20	Nriagu 1980

Zn Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
1.48	72	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	23°C, HD=20	Nriagu 1980
1.27	96	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	23°C, HD=20	Nriagu 1980
5.29	24, 48	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	23°C, HD=100	Nriagu 1980
1.27	72, 96	Mollusc (<i>Heliosoma companulata</i>)	LC ₅₀	23°C, HD=100	Nriagu 1980
14	96	Snail, bladder	LC ₅₀	-	WQC 1972
13.5	48	Snail (<i>Gonobasis livescens</i>)	LC ₅₀	HD=154	AWQC 1980
2.3	48	Snail (<i>Physa integra</i>)	LC ₅₀	HD=154	AWQC 1980
4.15	48	Snail (<i>Lymnea</i> sp.)	LC ₅₀	HD=154	AWQC 1980
10	96	Worm (<i>Limnodrilus</i>)	LC ₅₀	pH=5.8 to 9.7	Whitley 1968
0.12	24	Worm (<i>Tubiflex tubiflex</i>)	LC ₅₀	20°C, distilled water	Nriagu 1980
0.11	48	Worm (<i>Tubiflex tubiflex</i>)	LC ₅₀	20°C, distilled water	Nriagu 1980
4.62	24	Worm (<i>Tubiflex tubiflex</i>)	LC ₅₀	20°C, HD=34.2	Nriagu 1980
2.98	48	Worm (<i>Tubiflex tubiflex</i>)	LC ₅₀	20°C, HD=34.2	Nriagu 1980
75.8	24	Worm (<i>Tubiflex tubiflex</i>)	LC ₅₀	20°C, HD=261	Nriagu 1980
60.2	48	Worm (<i>Tubiflex tubiflex</i>)	LC ₅₀	20°C, HD=261	Nriagu 1980

6.2.3.2 Saltwater toxicity.

Zn Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
<u>Fish Toxicity Tests</u>					
11.5 to 14.0	tns	<i>Aldrichetta fosteri</i>	LC ₅₀	flow- through	JWPCF 1977
6.0	8	Atlantic salmon parr (<i>Salmo salar</i>)	LC ₅₀	flow- through, HD=14	Carson 1972
2.313	22	Atlantic salmon parr (<i>Salmo salar</i>)	LC ₅₀	flow- through, HD=14	Carson 1972
0.812	84	Atlantic salmon parr (<i>Salmo salar</i>)	LC ₅₀	flow- through, HD=14	Carson 1972
6.0 to 35	48	Atlantic salmon smelt	LC ₅₀	-	AWQC 1980
60	96	<i>Fundulus heterocli- tus</i>	LC ₅₀	-	JWPCF 1979

Zn Conc. (mg/L)	Species	Result	Reference
<u>Plants</u>			
0.4	Algae (<i>Amphidinium carteri</i>)	growth inhibition	AWQC 1980
0.20	Algae (<i>Phaeodactylum tricornutum</i>)	growth inhibition	AWQC 1980
0.4	Algae (<i>Thalassiosira pseudonana</i>)	growth inhibition	AWQC 1980
0.25	Kelp (<i>Laminaria digitata</i>)	growth inhibition	AWQC 1980

Zn Conc. (mg/L)	Time (hours)	Species	Result	Reference
<u>Invertebrates</u>				
0.195	240	Hardshell clam (<i>Mercenaria mercenaria</i>), larvae	LC ₅₀	AWQC 1980
7.7	96	Soft shell clam (<i>Mya arenaria</i>)	LC ₅₀	AWQC 1980
3.1	168	Soft shell clam (<i>Mya arenaria</i>)	LC ₅₀	AWQC 1980
257.5	45	Cockle	LC ₅₀	Portman 1976
1.45	96	Copepod (<i>Nitocra spinipes</i>)	LC ₅₀	AWQC 1980
0.456	96	Crab (<i>Cancer magister</i>), larvae	LC ₅₀	JWPCF 1982
14.5	48	Crab (unspecified)	EC ₅₀	WQC 1972
0.4	96	Decapod (<i>Pagurus longicarpus</i>)	LC ₅₀	AWQC 1980
50	96	Gastropod (<i>Nassarius obsoletus</i>)	LC ₅₀	JWPCF 1979
10	50	Isopod (<i>Idotea baltica</i>)	LC ₇₅	AWQC 1976
10	72	Isopod (<i>Jaera albitrons</i>)	LC ₈₀	AWQC 1976
0.175	48	Mussel embryos (<i>Mytilus edulis</i>)	EC ₅₀	JWPCF 1982
0.5	48	Oyster larvae (<i>Crassostrea virginica</i>)	LC ₁₀₀	AWQC 1980
0.1 to 0.15	tns	Pacific oyster	decrease in growth	Jorgensen 1979
0.075	192	Oyster (<i>Crassostrea margaritacea</i>)	50 percent reduction in growth	JWPCF 1983
0.119	48	Oyster embryos (<i>Crassostrea gigas</i>)	EC ₅₀	JWPCF 1982
1.8	96	Polychaete (<i>Neanthes arenaceodentata</i>)	LC ₅₀	JWPCF 1979
2.7	96	Polychaete (<i>Ophryotrocha diadema</i>)	LC ₅₀	JWPCF 1979
3.5	96	Polychaete (<i>Capitella capitata</i>)	LC ₅₀	JWPCF 1977

Zn Conc. (mg/L)	Time (hours)	Species	Result	Reference
7.1	96	Polychaete (<i>Ctenodrilus serratus</i>)	LC ₅₀	JWPCF 1979
8.1	96	Polychaete (<i>Nereis virens</i>)	LC ₅₀	JWPCF 1979
10.7	96	Polychaete (<i>Capitella capitata</i>)	LC ₅₀	JWPCF 1979
1.0	312	Polychaete (<i>Ophryotrocha diadema</i>)	LC ₅₀	AWQC 1980
9.5	48	Prawn	LC ₅₀	Portman 1970
2.6	168	Sandworm (<i>Nereis virens</i>)	LC ₅₀	AWQC 1980
39	96	Sea star (<i>Asterias forbesi</i>)	LC ₅₀	JWPCF 1979
110	48	Shrimp	LC ₅₀	Portman 1970

6.2.4 Aquatic Studies. The toxicity of zinc sulphate can be correlated with a number of physical/chemical factors. The toxicity of zinc sulphate increases as (Nriagu 1980): the temperature increases, the pH goes down, the hardness decreases, the dissolved oxygen decreases, and the concentration of other metal ions goes up.

The mode of zinc toxicity in freshwater fish has at one time been attributed to the destruction of the gill epithelium and consequent hypoxia (lack of oxygen). Recent studies have demonstrated that metabolically active tissues affected by an excess of zinc ions are unable to utilize oxygen; therefore, gas exchange is apparently disrupted both at the surface of the gill and at internal tissue sites (Spear 1981; Skidmore 1967; Burton 1972). One study showed that, on a long-term basis, the plasma glucose levels were affected in rainbow trout (1.12 ppm, 63 days), leading to the observation that zinc may also act on organs such as the liver (Watson 1971).

The toxicity of zinc sulphate to Atlantic salmon is somewhat lower in the presence of humic acids which bind some of the zinc ion (Carson 1972; Wildish 1971). A study of the life cycle of the fathead minnow showed that the most sensitive indicators of zinc toxicity were egg adhesiveness and fragility. These were most affected at 145 µg/L (zinc from zinc sulphate) but not affected at 78 µg/L (Benoit 1978). A study of the uptake of zinc into gills showed a direct correlation with temperature (Hodson 1975). A 134-day bioassay on guppies showed that the greatest zinc body burden occurred in the

5-day juveniles and during the onset of pregnancy. The study also showed that females actively transmitted zinc to embryos. An exposure of 0.607 mg/L (zinc) reduced the net weight of the female by 40 percent over the 134-day period. The most sensitive indicator of toxicity was sexual maturity manifested by fewer births (up to 50 percent decrease) and time from birth when the first brood was produced. The data suggest that at least two modes of zinc regulation exist among fishes (Pierson 1980).

6.3 Mammalian and Avian Toxicology

Zinc is a dietary requirement of all poultry and livestock; in low quantities, it is relatively nontoxic for animals (WQC 1972). The following are some specific toxicities:

Conc. (ppm)	Species	Result	Reference
1000 (Zn)	Swine	nontoxic	WQC 1972
2000 (Zn)	Swine	toxic	WQC 1972
2300 mg/L (Zn)	Chickens	reduced egg production and body weight	WQC 1972

6.4 Other Land and Air Toxicity

Zn Conc. (in soil or soil water) (mg/L)	Time (hours)	Species	Result	Reference
0.5	100 days	Kauri pine	growth diminished; toxic symptoms	Jorgensen 1979
16 to 32		Sugar beet	iron deficiencies	WQC 1972
25		Oats	toxic	WQC 1972
0.4		Soybean (Peking)	lethal	WQC 1972
1.8	40	Fungus	LD ₅₀	Nowasielski 1971
500	-	Field corn	42 percent decrease in yield	Zinc 1979
500	-	Sorghum	80 percent decrease in yield	Zinc 1979

Zn Conc. (in soil or soil water) (mg/L)	Time (hours)	Species	Result	Reference
500	-	Barley	76 percent decrease in yield	Zinc 1979
500	-	Wheat	45 percent decrease in yield	Zinc 1979
500	-	Field beans	10 percent decrease in yield	Zinc 1979
500	-	Alfalfa	22 percent decrease in yield	Zinc 1979
500	-	Clover	9 percent decrease in yield	Zinc 1979
500	-	Pea	8 percent decrease in yield	Zinc 1979
500	-	Lettuce	31 percent decrease in yield	Zinc 1979
500	-	Spinach	32 percent decrease in yield	Zinc 1979
500	-	Potato	0 percent decrease in yield	Zinc 1979
500	-	Sugar beet	40 percent decrease in yield	Zinc 1979
500	-	Tomato	26 percent decrease in yield	Zinc 1979

The toxicity of zinc in soils is related to soil pH (lower pH, more toxic); treating acid soil with lime has a large effect in reducing zinc toxicity. More zinc is required to produce toxic effects in clay or peat soils than in sandy soils (WQC 1972). One

study showed a reduction in microflora on the leaves of pine and cabbage when treated with zinc (Gingell 1976).

Concentrations over 20 ppm show a toxic effect on activated sludge; 1000 ppm severely inhibits sewage digestion (Schroeder 1975).

6.5 Long-term Fate and Effects

6.5.1 Bioaccumulation. Zinc is known to accumulate in various tissues. The bioconcentration of zinc in various marine species has been measured as follows (Nriagu 1980; Spear 1981):

	Bioconcentration Factor
Algae	530 to 64 000
Crustacea	85 to 1 500 000
Echinodermata	15 to 500
Mollusca	1525 to 4 000 000
Teleostei	3 to 15 000

The bioconcentration factors for freshwater species are known to be similar (Chapman 1973).

7 HUMAN HEALTH

Limited review data on the toxicity of zinc sulphate were found in the literature. Irritation effects as a result of skin and eye exposure to the solid and dust have been reported. Ingestion of small amounts may produce mild gastrointestinal disorders; larger amounts, if ingested, may cause corrosion and perforation of the gastrointestinal tract. The compound has been reported as producing neoplasms in rabbits and as having teratogenic effects in pregnant hamsters. No data were found in the literature concerning the potential mutagenic effects of zinc sulphate. The chemical has been reported in the EPA TSCA Inventory.

The toxicological data summarized here have been extracted from reliable standard reference sources. A number of reviews on zinc toxicity have been published (Nriagu 1980; Zinc 1979). 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 teratogenicity 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 zinc sulphate were encountered in the literature.

Effect	Origin	Level	Reference
<u>Summary Human Toxicities</u>			
Probable oral lethal dose	-	50 to 500 mg/kg; between 1 teaspoonful and 1 ounce for a 70 kg person (150 lb.)	TDB (on-line) 1981
TD _{LO} , systemic toxic effects and blood pressure effects	-	106 mg/kg	RTECS 1979
TD _{LO} , gastro-intestinal effects	-	45 mg/kg (7 d)	TDB (on-line) 1981

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Workers working in uncontrolled levels of fumes or dusts of zinc sulphate developed dermatitis and boils. Such findings did not occur until exposure had lasted more than 6 months.	TDB (on-line) 1981; Athanassiadias 1969
Unspecified	Solid and dust are irritating to skin.	CHRIS 1978

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
High concentration	May cause lens opacities and reduced intraocular pressure, as well as deposition of pigment on the posterior surface of the cornea. Symptoms sometimes resemble those of severe acute attacks of angle-closure glaucoma.	TDB (on-line) 1981
Unspecified	Workers working in uncontrolled levels of dusts and fumes developed conjunctivitis. Such findings did not occur until exposure had lasted more than 6 months.	TDB (on-line) 1981
Unspecified	Exposure to zinc salts commonly results in epithelial erosion and stromal opacification of cornea which is sometimes accompanied by anterior subcapsular lens changes. These effects are due to the precipitation of protein caused by zinc.	TDB (on-line) 1981

Exposure Level (and Duration)	Effects	Reference
Unspecified	Solid and dust are irritating to eyes.	CHRIS 1978
SPECIES: Cattle		
20 percent solution	Applied to cattle corneas; affected permeability of epithelium only slightly and at a slow rate.	TDB (on-line) 1981
SPECIES: Pig		
Unspecified	Experiment performed on enucleated pig eyes produced grayish, but not white opacity of the cornea.	TDB (on-line) 1981
SPECIES: Rabbit		
420 µg	Moderate irritation.	RTECS 1979

7.3 Threshold Perception Properties

7.3.1 Odour. Odour Characteristics: Odourless (CHRIS 1978).

7.3.2 Taste. Taste Characteristics: Astringent (TDB (on-line) 1981).

Parameter	Media	Concentration	Reference
Taste Threshold Concentration	-	15 ppm	Patty 1981
Metallic Taste	in water	40 ppm	Patty 1981

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Human		
Unspecified	If inhaled, will cause coughing or difficult breathing.	CHRIS 1978
<u>Chronic Exposures</u>		
SPECIES: Human		
Unspecified	Exposure to mists containing sulphuric acid and zinc sulphate evolved during electrolytic manufacturing of zinc has been reported to produce irritation of the respiratory and digestive systems and dental deterioration.	TDB (on-line) 1981
Unspecified	Workers working in uncontrolled levels of fumes or dusts of zinc sulphate developed dermatitis, boils, conjunctivitis and gastrointestinal disturbances. Such findings did not occur until exposure had lasted more than 6 months.	TDB (on-line) 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Human		
30 g	Has caused fatalities.	TDB (on-line) 1981

Exposure Level (and Duration)	Effects	Reference
0.6 to 2.0 g	An emetic. Overdose may cause corrosion and inflammation of mucous membranes of mouth and stomach. Ulcers may form in stomach and often lead to perforation. Burning pain in throat and stomach, vomiting, diarrhea, leg cramps, hypotension and cold sweat.	TDB (on-line) 1981
50 to 500 mg/kg	Probable oral lethal dose. (Between 1 teaspoonful and 1 ounce for a 70 kg (150 lb.) man).	TDB (on-line) 1981
106 mg/kg	TD _{LO} , produced systemic effects and blood pressure effects.	TDB (on-line) 1981
SPECIES: Cattle		
Unspecified	Large doses of zinc salts produce general signs of acute metal poisoning, violent vomiting, purgation, evidence of abdominal pain, and collapse. Cattle show dramatic drop in milk yield. Some animals become somnolent and develop paresis.	TDB (on-line) 1981
SPECIES: Chicken		
2230 ppm	Decreased water consumption, egg production and body weight.	TDB (on-line) 1981
SPECIES: Rabbit		
2000 mg/m ³	LD _{LO}	RTECS 1979
SPECIES: Rat		
2200 mg/m ³	LD _{LO}	RTECS 1979
<u>Chronic Exposures</u>		
SPECIES: Human		
45 mg/m ³ (7 d) continuous	TD _{LO} , gastrointestinal effects.	RTECS 1979

7.4.3 Teratogenicity and Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Hamster		
2 mg/kg	TD _{LO} , teratogen for 8-day pregnant animals. Intravenous administration.	RTECS 1979
SPECIES: Rabbit		
6170 µg/kg (5 d) continuous	Subcutaneous administration. Neoplasms.	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 nature have their sources indicated.

7.5.1 Inhalation.

1. Irritation of the nose and throat (CHRIS 1978).
2. Irritation of the respiratory system (TDB (on-line) 1981).

7.5.2 Ingestion.

1. Burning pain in throat and stomach (TDB (on-line) 1981).
2. Corrosion and inflammation of mucous membranes of the mouth and stomach (TDB (on-line) 1981).
3. Vomiting (TDB (on-line) 1981).
4. Diarrhea (TDB (on-line) 1981).
5. Leg cramps (TDB (on-line) 1981).
6. Hypotension (TDB (on-line) 1981).
7. Cold sweats (TDB (on-line) 1981).
8. Tenesmus (TDB (on-line) 1981).
9. Retching (TDB (on-line) 1981).
10. Anuria (TDB (on-line) 1981).
11. Hypoglycemia (TDB (on-line) 1981).

12. Hepatic and renal damage (TDB (on-line) 1981).
13. Collapse and convulsions (TDB (on-line) 1981).
14. Death.

7.5.3 Skin Contact.

1. Irritation.
2. Dermatitis (TDB (on-line) 1981).
3. Boils (TDB (on-line) 1981).

7.5.4 Eye Contact.

1. Irritation (TDB (on-line) 1981).
2. Conjunctivitis (TDB (on-line) 1981).
3. Epithelial erosion (TDB (on-line) 1981).
4. Reduced intraocular pressure (TDB (on-line) 1981).
5. Glaucoma (TDB (on-line) 1981).
6. Deposition of pigmentation on posterior of the eye (TDB (on-line) 1981).
7. Stomal opacification of cornea (TDB (on-line) 1981).
8. Lens opacities (TDB (on-line) 1981).

7.6 Human Toxicity to Decay or Combustion Products

At 767°C, zinc sulphate decomposes to ZnO (zinc oxide) and SO₃ (sulphur trioxide) (Partington 1958). The oxide of zinc is a white or yellowish-white, nonflammable powder which sublimates under normal pressure and has a melting point of 1975°C. Metal fume fever may result from the inhalation of zinc oxide fume. The symptoms include fever, chills, muscular pain, nausea and vomiting; however, complete recovery occurs in 24 to 48 hours. The same effects may also result from breathing finely divided zinc oxide dust (Doc. TLV 1981). The TLV® for zinc oxide fume is 5 ppm (8 h - TWA) and 10 ppm (STEL). Zinc oxide dust is classified as a nuisance particulate (TLV 1983).

Ordinarily, sulphur trioxide vapour is rapidly converted in air to a mist of sulphuric acid by reaction with atmospheric moisture. Inhalation of sulphuric acid mist can produce pulmonary irritation, cough, bronchoconstriction, and pulmonary irritation. The TLV® for sulphuric acid is 1 mg/m³ (TLV 1983).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Zinc Sulphate with Chemical Groups

CHEMICAL GROUPS	SPECIFIC CHEMICAL OR CHEMICAL GROUP											SPECIFICS	REFERENCE
	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION	FORMATION OF POLYMERIZATION	FORMATION OF TOXIC FUMES	OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	NON-HAZARDOUS REACTION		
Epoxides	•			•								Polymerization can occur.	EPA 600/2-80-076
Explosives	•	•											EPA 600/2-80-076
Organic Peroxides	•				•							Decomposition of peroxides occurs with evolution of oxygen and carbon dioxide.	EPA 600/2-80-076
Polymers	•			•								Polymerization can occur.	EPA 600/2-80-076
Water								•					EPA 600/2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be discrepancies between different sources of information. It is recognized that counter-measures 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. Zinc sulphate is a noncombustible material. It emits toxic vapours when heated to decomposition (OHM-TADS 1981).

9.1.2 Fire Extinguishing Agent. Use water spray to cool containers involved in a fire. Move containers from fire area if this can be done without risk (ERG 1980).

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.

9.1.3.2 Spills on land. If spilled in a solid form, collect or shovel material in suitable container for recovery or disposal (avoid dusting) (Virginia MSDS).

If spilled in solution form, contain if possible by forming mechanical barriers to prevent spreading (EPA 670/2-75-042). The liquid may be adsorbed on sand or other sorbent material and shoveled into containers for disposal (ERG 1980). Lime could be used as a neutralizing agent (OHM-TADS 1981).

9.1.3.3 Spills in water. Contain if possible. Application of a sodium sulphide solution to the solubilized portion to precipitate the zinc is recommended. Addition of dilute acid or removable strong acid to neutralize the spill is also recommended. Then use mechanical dredges or lifts to remove immobilized masses of pollutants and precipitates (EPA 670/2-75-042). Treatment with a cation exchange resin or lime could also be used to remove the zinc (OHM-TADS 1981).

For treatment of contaminated water, gravity separation of solids followed by precipitation (pH 11.0) of zinc with a mixture (50/50) of soda ash and lime is recommended. The solids are removed by settling and the water is neutralized to pH 7.0 with hydrochloric acid prior to discharge. If necessary, the water may pass through dual media

filtration prior to neutralization with HCl (EPA 600/2-77-227; Rock 1971). NTA (the trisodium salt of nitrilotriacetic acid) was found to be a useful sequestering agent to protect brook trout from zinc toxicity up to 33 times the normal threshold toxicity (Sprague 1968).

9.1.4 Disposal. Zinc sulphate must never be discharged directly into sewers or surface waters. Recovered zinc sulphate may be recycled by the manufacturer.

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 zinc sulphate (Virginia MSDS):

- Chemical safety goggles and a dust mask should be worn.
- Rubber is recommended for gloves.
- Eye wash stations should be readily available in areas of use and spill situations.

9.1.6 Storage Precautions. Store in a dry location. Avoid excessive heat and moisture (Virginia MSDS).

10 PREVIOUS SPILL EXPERIENCE

10.1 General

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.

10.2 Trailer Accident (HMN 1981)

A semitrailer, carrying approximately 20 tonnes of zinc sulphate fertilizer packaged in paper bags, crashed on a highway and spilled some of its load. Response personnel arrived at the site and vacuumed the spilled material from the broken bags into barrels. The broken paper bags were burned and the area washed down with water. Some response personnel suffered ill effects - vomiting, nausea, respiratory distress and skin irritation - during cleanup operations.

Although this material is used routinely as a fertilizer, it may still be hazardous in high exposure circumstances such as spills. Personal protective equipment should be used by cleanup personnel to reduce exposure. Furthermore, disposal of contaminated bags by burning should be done only after considering possible air contamination by dust, decomposition products and other components of the mixture.

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 standard equipped chemical laboratory distant from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. This source 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, these have been presented as well.

11.1 Quantitative Method for the Detection of Zinc Sulphate in Air

11.1.1 Atomic Absorption Spectrophotometry (NIOSH 1977). A range of 4.2 to 42 $\mu\text{g}/\text{m}^3$ (1 to 10 ppb) of zinc sulphate as zinc may be determined by atomic absorption spectrophotometry.

A known volume of air is drawn through a 37 mm diameter cellulose-ester filter of 0.8 μ pore size housed in a two-piece filter cassette holder. A sample size of 180 L at a flow of 1.5 L/min is recommended.

The filter sample is transferred to a clean 125 mL beaker and 6.0 mL of concentrated nitric acid are added. The beaker is covered with a watch glass and heated to 140°C on a hotplate in a fumehood. The heating is continued until the filter dissolves and a slightly yellow solution is produced. Once digestion is complete (clear solution), the watch glass is removed and the sample allowed to cool. A 1 mL volume of concentrated nitric acid and 3 mL of distilled water are added to the beaker. The solution is quantitatively transferred to a 10 mL volumetric flask and taken to volume with distilled water.

A 2 mL volume of the sample is aspirated into the flame of a suitable atomic absorption spectrophotometer equipped with air-acetylene and nitrous oxide-acetylene

burner heads, a deuterium hollow cathode lamp, two-stage regulators for air, acetylene and nitrous oxide, as well as heating tape and rheostat for nitrous oxide regulator.

The absorbance is determined at 213.9 nm and the concentration determined using a calibration curve.

11.2 Qualitative Method for the Detection of Zinc Sulphate in Air

Zinc sulphate in air may be determined as zinc by a colourimetric test. The sample is collected and digested (see Section 11.1.1). A 5 drop volume of sample is placed in a test tube and is made strongly basic with the addition of 2 M sodium hydroxide. The mixture is then centrifuged and 1 drop of clear supernatant placed in the centre of a circle of dithizone paper. A purple-red ring which forms at the edge of the drop indicates zinc. The dithizone paper is prepared by dipping qualitative filter prepared into a saturated solution of dithizone in acetone (Welcher 1955).

11.3 Quantitative Method for the Detection of Zinc Sulphate in Water

11.3.1 Colourimetric (ASTM 1979). A range of 0.02 to 5 mg/L (ppm) of zinc sulphate as zinc in water may be determined colourimetrically.

A minimum volume of 2 L of representative sample is collected in an appropriate container. A 50 mL volume of well shaken sample is transferred to a 250 mL beaker. A 1 mL volume of concentrated hydrochloric acid is added and the solution heated to boiling. The boiling is continued for 5 minutes. The solution is allowed to cool and sodium hydroxide (240 g/L) solution added to obtain a pH of 7. The solution is transferred to a 50 mL volumetric flask and diluted to volume with water. A 10 mL aliquot of diluted sample is transferred to a 100 mL Erlenmeyer flask. The following reagents are added, in order, mixing after each addition: 0.5 g of sodium ascorbate, 1 mL of cyanide solution, 5 mL of buffer solution, 3 mL of zincon solution, and 3 mL of chloral hydrate solution.

The reagents are prepared in the following manner. The cyanide solution is prepared by dissolving 1.0 g of potassium cyanide in 50 mL of water and diluting to 100 mL. This solution must be kept in a well capped bottle and handled with extreme care. The buffer solution is prepared by diluting 213 mL of 40 percent w/v sodium hydroxide solution in 600 mL water. A 37.3 g mass of potassium chloride and 31.0 g of boric acid are added, dissolved, and the mixture taken to 1 L with water. The zincon solution is prepared by dissolving 0.260 g of powdered 2-carboxy-2'-hydroxy-5-sulfoformazylbenzene in 100 mL methanol by heating to below 50°C and stirring until

solution is complete. The solution is allowed to cool and quantitatively transferred to a 200 mL volumetric flask. The rinsings are added to the volumetric flask.

The solution is taken to volume with methanol and the solution stored in an amber bottle and preferably refrigerated. The absorbance of the colour-developed sample is determined on a suitable spectrophotometer at 620 nm using 1 cm matched cells. The sample concentration is determined using a calibration curve.

11.4 Qualitative Method for the Detection of Zinc Sulphate in Water

Zinc sulphate in water may be determined as zinc by a colourimetric test. The sample is collected as described in Section 11.3.1. A 5 drop volume of sample is placed in a test tube and is made strongly basic with the addition of 2 M sodium hydroxide. The mixture is then centrifuged and 1 drop of clear supernatant placed in the centre of a circle of dithizone paper. A purple-red ring which forms at the edge of the drop indicates zinc. The dithizone paper is prepared by dipping qualitative filter paper into a saturated solution of dithizone in acetone (Welcher 1955).

11.5 Quantitative Method for the Detection of Zinc Sulphate in Soil

11.5.1 Spectrophotometric (Hesse 1972). Although this method is used specifically for the determination of zinc, it may also be used for zinc sulphate. A range of 0 to 100 ppm of zinc may be determined in soil by spectrophotometric measurement. The range may be extended by sample dilution.

A 1.0 g sample of 0.15 mm soil is placed in a 250 mL beaker and 20 mL of concentrated nitric acid are added. The beaker is covered and heated using low heat. A 10 mL volume of 60 percent perchloric acid is added and the mixture digested until dense white fumes appear. The sides of the beaker are washed with a small portion of 60 percent perchloric acid. The mixture is digested for 15 minutes to dehydrate the silica, cooled, and diluted with 25 mL of warm water. The mixture is then filtered through a Whatman 41 filter paper and the filtrate collected in a 100 mL volumetric flask. The silica residue is washed with 0.5 M hydrochloric acid and the wash added to the flask. The solution is taken to volume with 0.5 M hydrochloric acid.

A suitable aliquot of digest is transferred to a 125 mL separatory funnel. A 5 mL volume of ammonium citrate buffer is added. It is prepared by dissolving 225 g of ammonium citrate in 1 L of water. The pH of the buffer is adjusted to 8.5 with 40 mL of strong ammonium hydroxide solution. The mixture is extracted with 20 mL portions of dithizone in carbon tetrachloride.

Dithizone in carbon tetrachloride is prepared by dissolving 0.25 g diphenylthiocarbazone in 1 L of pure carbon tetrachloride. A 2 mL volume of the mixture is shaken for 5 minutes. The carbon tetrachloride layer is discarded and the solution is extracted with 50 mL portions of pure carbon tetrachloride until the extract is clear green.

A 500 mL volume of carbon tetrachloride and 50 mL of 1.0 M hydrochloric acid are added and the mixture shaken. The aqueous layer is discarded and the organic layer is diluted to 2 L. A 25 mL volume of water partly saturated with sulphur dioxide is added. The prepared dithizone in carbon tetrachloride is stored in an amber bottle.

The ammonium citrate buffer preparation is continued in the following manner. The pH-adjusted buffer is extracted with more 20 mL portions of dithizone in carbon tetrachloride until the organic phase remains green and the aqueous phase remains orange.

The aqueous phase is extracted with pure carbon tetrachloride; a suitable volume of ammonium hydroxide is used to adjust the pH to 2.5.

The sample (digest) treatment is continued in the following manner. Ammonium hydroxide (0.1 mL) solution is added to obtain a pH of 2.5. Then 3 drops of bromothymol blue indicator plus 5 mL of dithizone solution are added and the mixture shaken for 5 minutes. The aqueous phase is run into a clean 125 mL separatory funnel. The sample is then re-extracted and the two extracts combined. The carbon tetrachloride phases are discarded.

A 5 mL volume of ammonium citrate buffer solution is added to the combined aqueous extracts and the pH adjusted to 8.3 with 0.1 M ammonium hydroxide solution, using phenolphthalein as indicator. The zinc is extracted with two 10 mL portions of dithizone solution. The aqueous phase becomes orange in colour when all the zinc has been extracted.

The aqueous phase is extracted once more with pure carbon tetrachloride. The combined organic phases are placed in a clean 125 mL separatory funnel and shaken for 2 minutes with 50 mL of 0.02 M hydrochloric acid. The organic phase is discarded and the aqueous phase is washed with a 10 mL portion of pure carbon tetrachloride.

A 5 mL volume of citrate buffer solution is added and the pH adjusted to 8.3 with 0.1 M ammonium hydroxide. A 10 mL volume of dithizone solution and 10 mL of carbonate solution are added and the mixture shaken for 2 minutes.

The carbonate solution is prepared by dissolving 0.2 g of sodium diethyldithiocarbonate in 100 mL of water and filtering into a separatory funnel. The solution is

shaken with 5 mL of pure carbon tetrachloride to remove any copper. The aqueous phase is stored in a dark bottle.

The sample treatment continues in the following manner. The organic phase is transferred to a clean 125 mL separatory funnel and shaken with 25 mL of 0.01 M ammonium hydroxide solution. A 5 mL volume of the organic phase containing the zinc dithizonate complex is placed in a matched 1 cm cell and the absorbance determined at 535 nm using a suitable spectrophotometer. The sample concentration is determined using a calibration curve.

11.6 Qualitative Method for the Detection of Zinc Sulphate in Soil

Zinc sulphate may be determined as sulphate in soil. The sample is collected as in Section 11.5.1 and extracted with 0.001 M lithium chloride, centrifuged, and filtered. A 1 mL volume of sample is acidified with 6 M hydrochloric acid followed by 1 mL of 1 M barium chloride solution. A finely divided white precipitate indicates the presence of sulphate ion (Welcher 1955).

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EnviroTIPS
Common Abbreviations

BOD	biological oxygen demand	°Be	degrees Baumé (density)
b.p.	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 Association
eV	electron volt	NIOSH	National Institute for Occupational Safety and Health
g	gram		
ha	hectare	nm	nanometre
Hg	mercury	o	ortho
IDLH	immediately dangerous to life and health	OC	open cup
Imp. gal.	imperial gallon	p	para
in.	inch	P _c	critical pressure
J	joule	PEL	permissible exposure level
kg	kilogram	pH	measure of acidity/alkalinity
kJ	kilojoule	ppb	parts per billion
km	kilometre	ppm	parts per million
kPa	kilopascal	P _s	standard pressure
kt	kilotonne	psi	pounds per square inch
L	litre	s	second
lb.	pound	STEL	short-term exposure limit
LC ₅₀	lethal concentration fifty	STIL	short-term inhalation limit
LC _{LO}	lethal concentration low	T _c	critical temperature
LD ₅₀	lethal dose fifty	TCLO	toxic concentration low
LD _{LO}	lethal dose low	Td	decomposition temperature
LEL	lower explosive limit	TDLO	toxic dose low
LFL	lower flammability limit	TL _m	median tolerance limit
m	metre	TLV	Threshold Limit Value
m	meta	Ts	standard temperature
M	molar	TWA	time weighted average
MAC	maximum acceptable concentration	UEL	upper explosive limit
max	maximum	UFL	upper flammability limit
mg	milligram	VMD	volume mean diameter
MIC	maximum immission concentration	v/v	volume per volume
min	minute or minimum	w/w	weight per weight
mm	millimetre		
µg	microgram		
µm	micrometre		