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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in planning for and designing countermeasures for spills of these substances. The manual has been reviewed by the 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. Readers are advised to consult other sources of information before making critical decisions. Mention of trade names or commercial products does not constitute endorsement for use.

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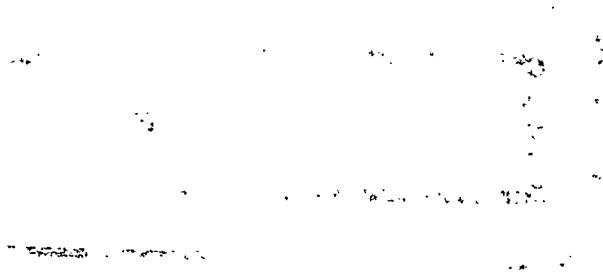
MERCURY

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUAL

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FOREWORD

The Environmental and Technical Information for Problem Spills (Enviro TIPS) 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 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. 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

MERCURY (Hg)

Silvery liquid with no odour

SYNONYMS

Metallic mercury, Quicksilver, Mercure (Fr.), Hydrargyrum, Liquid silver

IDENTIFICATION NUMBERS

UN No. 2809; CAS No. 7439-97-6; OHM-TADS No. 7216782; STCC No. 492369

GRADES & PURITIES

Available in commercial, instrument, redistilled, technical and triple distilled grades

IMMEDIATE CONCERNS

Fire: Not combustible. Vaporizes readily, forming toxic fumes

Human Health: Highly toxic by inhalation, skin absorption and eye and skin contact.
Toxicity by ingestion is thought to be minimal

Environmental: Not immediately harmful to aquatic life due to extremely low solubility.
Bacterial conversion to methylmercury greatly increases toxicity to aquatic life

PHYSICAL PROPERTY DATA

State: (15°C, 1 atm): liquid

Boiling Point: 356.9°C

Melting Point: -38.87°C

Flammability: not combustible

Vapour Pressure: 0.1601 Pa (20°C)

Specific Gravity (water = 1): 13.5939
(20°C/4°C)

Solubility (in water): 25 µg/L (25°C)

Behaviour (in water): sinks with no reaction

ENVIRONMENTAL CONCERNS

Mercury and its compounds can disperse throughout the environment and bioaccumulate in the food chain and ultimately in humans.

HUMAN HEALTH

TLV^o: 0.05 mg/m³ (skin, as Hg vapour)

IDLH: 28 mg/m³

Exposure Effects

Inhalation: Metallic taste, nausea, headache. Very high exposure may cause rapid and difficult breathing

Contact: Skin - may cause irritation and inflammation; mercury is absorbed through the skin. Eyes - irritation, watering, edema of eyelids

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "POISON". Notify distributor and environmental authorities. Contain spill, if safe to do so. Avoid contact with liquid and vapour. Keep contaminated water (and mercury itself) from entering sewers or watercourses.

Fire Control

Not combustible. Cool fire-exposed containers with water.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill. Remove material with vacuum-suction equipment. For very small spills, a suction bottle with a capillary tube can be used. Store in tightly sealed containers

Water: Contain with sand bag barrier, deep water pockets or natural barriers. Use suction hoses to remove trapped material

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Lustrous, silvery-white liquid with a slight blue tinge (CPTE 1974)
Usual shipping state	Liquid (CCD 1977)
Physical state at 15°C, 1 atm	Liquid
Melting point/Freezing point	-38.87°C (CPTE 1974)
Boiling point	356.9°C (Kirk-Othmer 1981)
Vapour pressure	0.1601 Pa (20°C) (CRC 1980)

Densities

Density	13.546 g/cm ³ (20°C) (CRC 1982) 13.595 g/cm ³ (0°C) (Kirk-Othmer 1981)
Specific gravity	13.5939 (20°/4°C) (CRC 1980)

Fire Properties

Flammability	Noncombustible (CCD 1977)
--------------	---------------------------

Other Properties

Atomic weight of pure substance	200.59 (CRC 1980)
Constituent components of typical commercial grade	99.9 percent mercury (Kirk-Othmer 1981)
Resistivity	95.8 μohm•cm (20°C) (Kirk-Othmer 1981)
Viscosity	1.55 mPa•s (20°C) (CPTE 1974)
Liquid interfacial tension with air	465 mN/m (20°C) (CPTE 1974) 480.3 mN/m (0°C) (Kirk-Othmer 1981)
Liquid interfacial tension with water	375 mN/m (20°C) (CRC 1980)
Latent heat of fusion	11.6 kJ/mole (at melting point) (CRC 1980)
Refractive index	1.6-1.9 (20°C) (Kirk-Othmer 1981)
Latent heat of sublimation	305.6 kJ/kg (25°C) (Lange's Handbook 1979)
Latent heat of vaporization	283.6 kJ/kg (25°C) (Lange's Handbook 1979) 271.96 kJ/kg (25°C) (Kirk-Othmer 1981)
Ionization potential	10.44 eV (Rosenstock 1977)

Heat capacity	
constant pressure (Cp)	Solid: 141 J/kg (-40°C) (Kirk-Othmer 1981) Liquid: 137.9 J/kg (25°C) (Kirk-Othmer 1981) Gas: 103.6 J/kg (357°C) (Kirk-Othmer 1981)
constant volume (Cv)	83.7 J/kg (25°C) (Merck 1976; Perry 1973)
Critical pressure	18 200 kPa (Lange's Handbook 1979) 74 200 kPa (Kirk-Othmer 1981)
Critical temperature	900°C (Lange's Handbook 1979) 1677°C (Kirk-Othmer 1981)
Triple point	-38.842°C (Kirk-Othmer 1981)
Coefficient of thermal expansion	$0.182 \times 10^{-3}/^{\circ}\text{C}$ (20°C) (Perry 1973; Kirk-Othmer 1981)
Thermal conductivity	0.092 W/(cm ² ·K) (25°C) (Kirk-Othmer 1981)
Diffusivity (in air)	0.112 cm ² /s (0°C) (Perry 1973)
Solubility	
In water	25 µg/L (25°C, air-free, neutral) (Linke 1958) 60 µg/L (30°C, contact with air) (Linke 1958) 300 µg/L (85°C, air-free) (Linke 1958) 600 µg/L (100°C, air-free) (Linke 1958)
In other common materials	Soluble in nitric acid; insoluble in dilute hydrochloric acid, hydrobromic acid, hydroiodic acid and cold sulphuric acid (CRC 1980)

Summary of Chemical/Physical Properties (Kirk-Othmer 1981; Cotton 1972)

Mercury is a dense, silvery-white metal that is in the liquid state at room temperature. Solid mercury is white; the vapour is colourless. It occurs in nature mainly in combination with sulphur; the most important commercial mineral is the red sulphide, cinnabar (HgS). The metal produced from the ore is called prime virgin mercury and is usually more than 99.9 percent pure. Mercury of higher purity is usually produced by multiple distillation or electrolytic refining. Generally, pure mercury has a clean, bright appearance. Almost all impurities, including amalgams, have a lower specific gravity and float on the surface, causing the bright, mirrorlike surface to become dull and black.

Mercury is relatively stable at ordinary temperatures and does not react noticeably with air, ammonia, carbon dioxide, nitrous oxide (N₂O), or oxygen. The reaction with oxygen proceeds at a faster and more useful rate at 300-350°C; however, at temperatures around 400°C and above, the stability relationship reverses and mercuric oxide (HgO) rapidly decomposes into the elements. Mercury combines readily at room temperature with halogens, sulphur, selenium and phosphorus. It reacts only slightly with

hydrochloric acid, but is attacked by concentrated sulphuric acid. Nitric acid, dilute or concentrated, dissolves mercury, forming mercurous (Hg_2^{++}) salts when mercury is in excess or no heat is applied, and mercuric (Hg^{++}) salts when excess acid is used or the mixture is heated. Mercury readily reacts with hydrogen sulphide in air.

Many metals react with mercury to form amalgams, some of which have definite compositions, e.g., Hg_2Na . Metals having good or excellent resistance to corrosion by amalgamation with mercury are vanadium, niobium, molybdenum, cesium, tantalum, tungsten and iron. This resistance is degraded at higher temperatures, even with iron.

One of the more important properties of mercury is its volume expansion, which is uniform over its entire liquid range. It also has a high surface tension and therefore does not wet and cling to glass. Mercury is rated as one of the best electrical conductors among metals; it also has a high thermal conductivity, permitting it to act as a coolant. Due to its high thermal-neutron-capture cross-section, it readily absorbs neutrons and acts as a shield for neutron-emitting devices.

Mercury's specific heat increases with increasing temperature in the solid phase and decreases nonuniformly in the liquid phase. It is interesting to note that the specific heat is the same at 210°C as it is at -75°C . The vapour pressure also behaves irregularly and is represented by the equations:

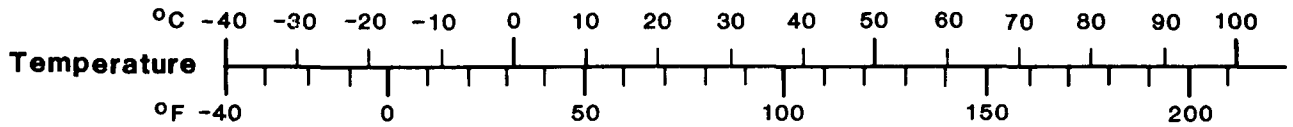
$$0-150^\circ\text{C} \quad \log P = -3212.5/T + 7.150$$

$$150-400^\circ\text{C} \quad \log P = -3141.33/T + 7.879 - 0.00019t$$

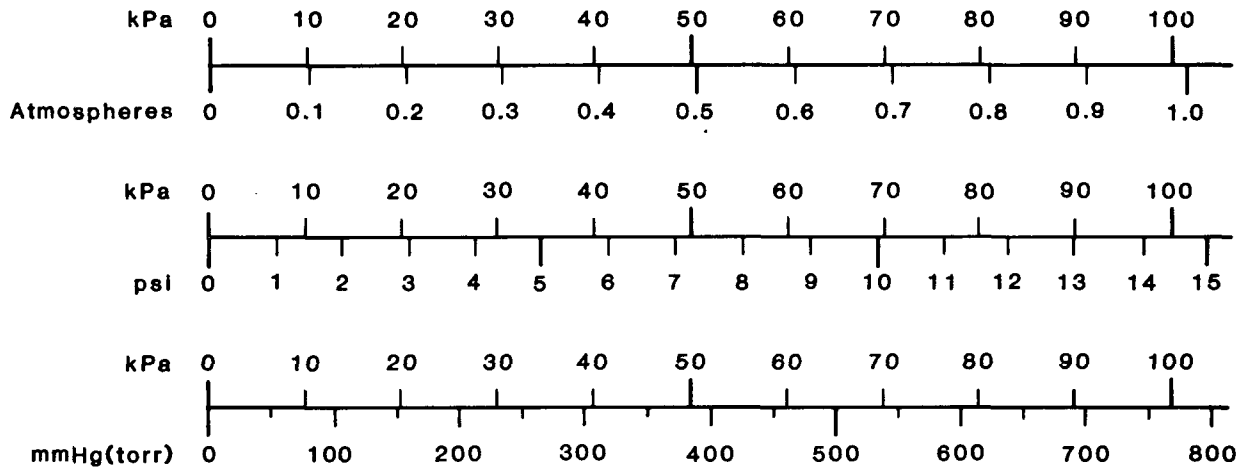
where P is vapour pressure in kPa, T is the absolute temperature in degrees Kelvin, and t is the temperature in degrees Celsius.

MERCURY

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa



Viscosity

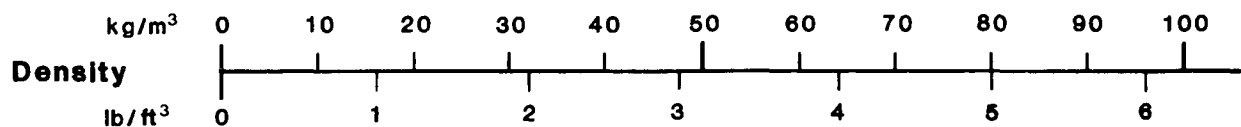
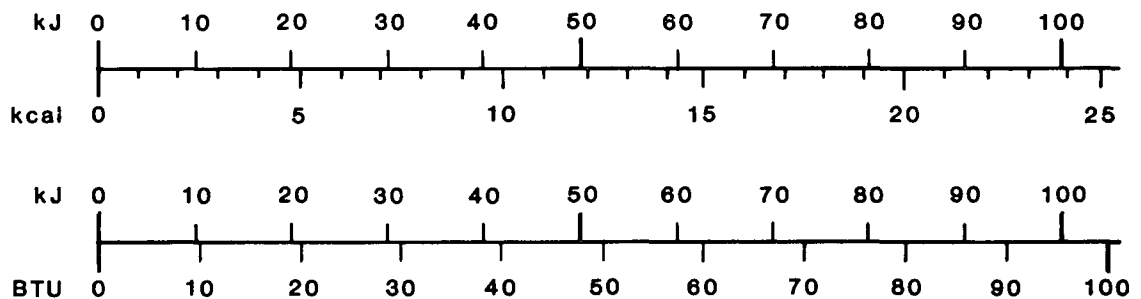
Dynamic 1 Pa·s = 1 000 centipoise (cP)

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



MERCURY

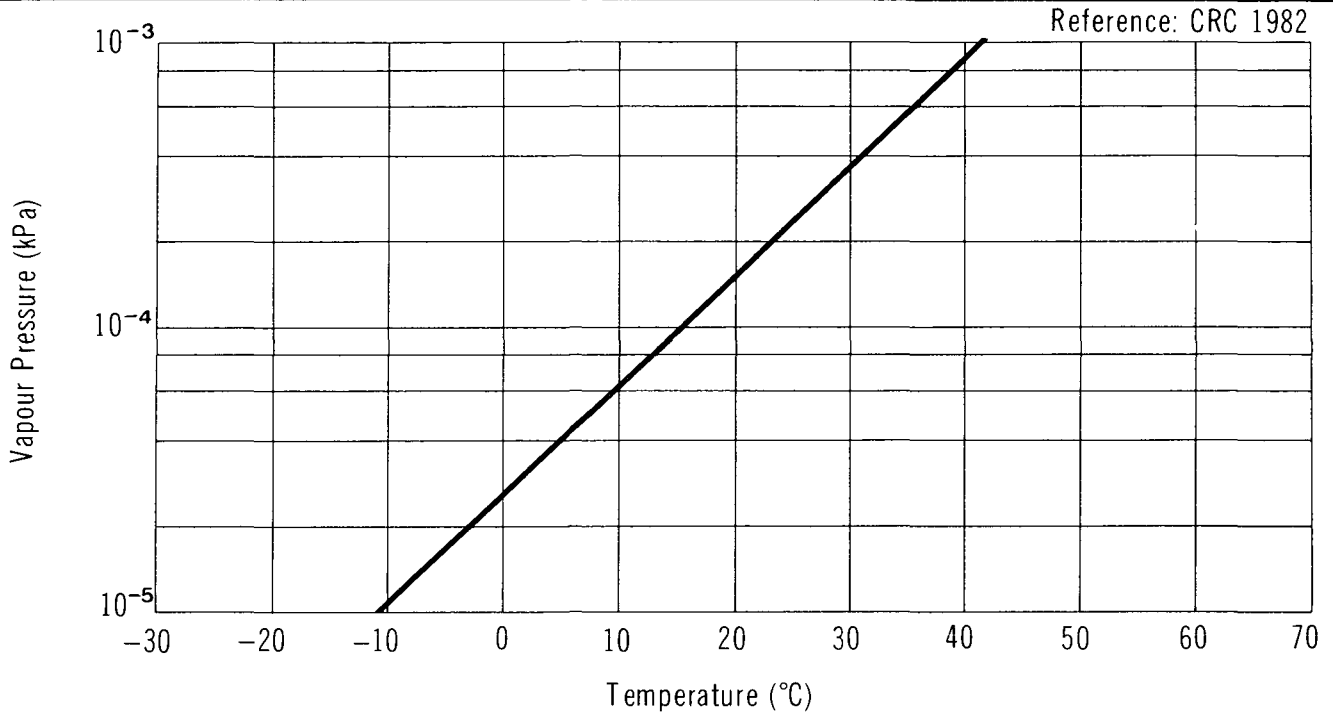
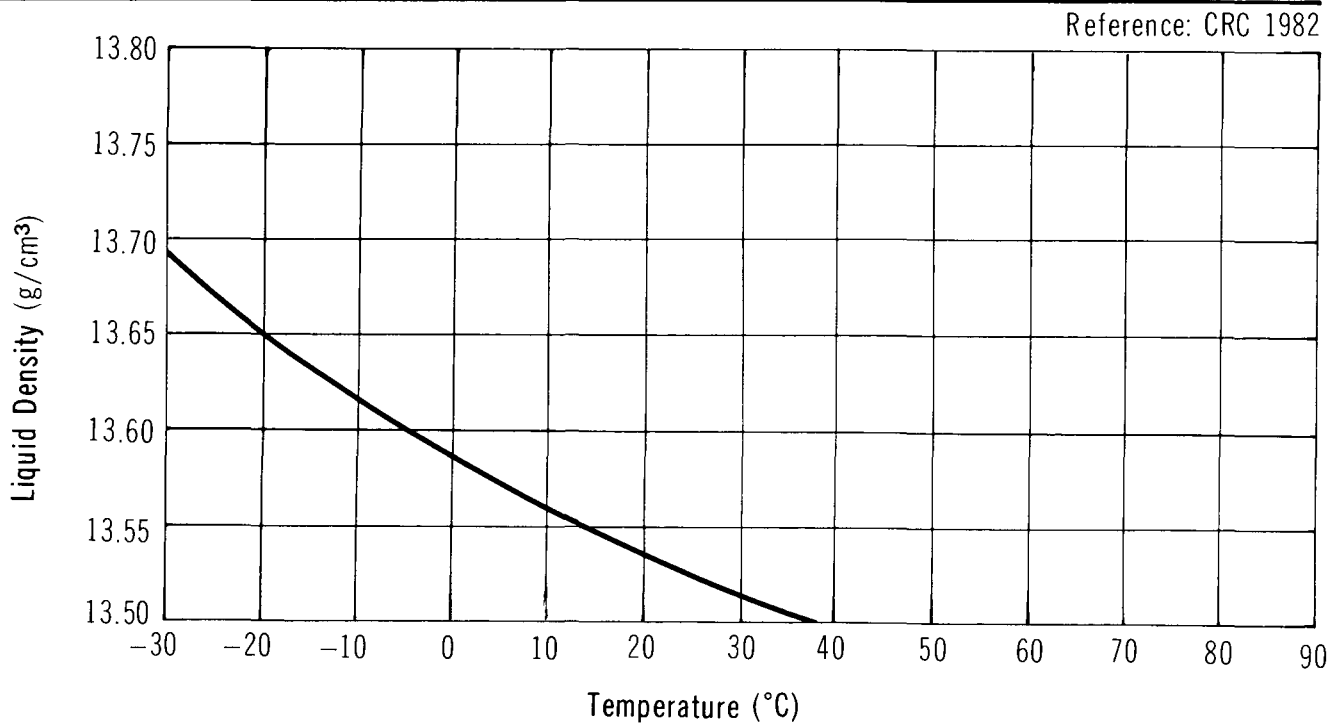
VAPOUR PRESSURE vs TEMPERATURE

FIGURE 2

MERCURY

LIQUID DENSITY vs TEMPERATURE

MERCURY

LIQUID VISCOSITY vs TEMPERATURE

Reference: CRC 1982

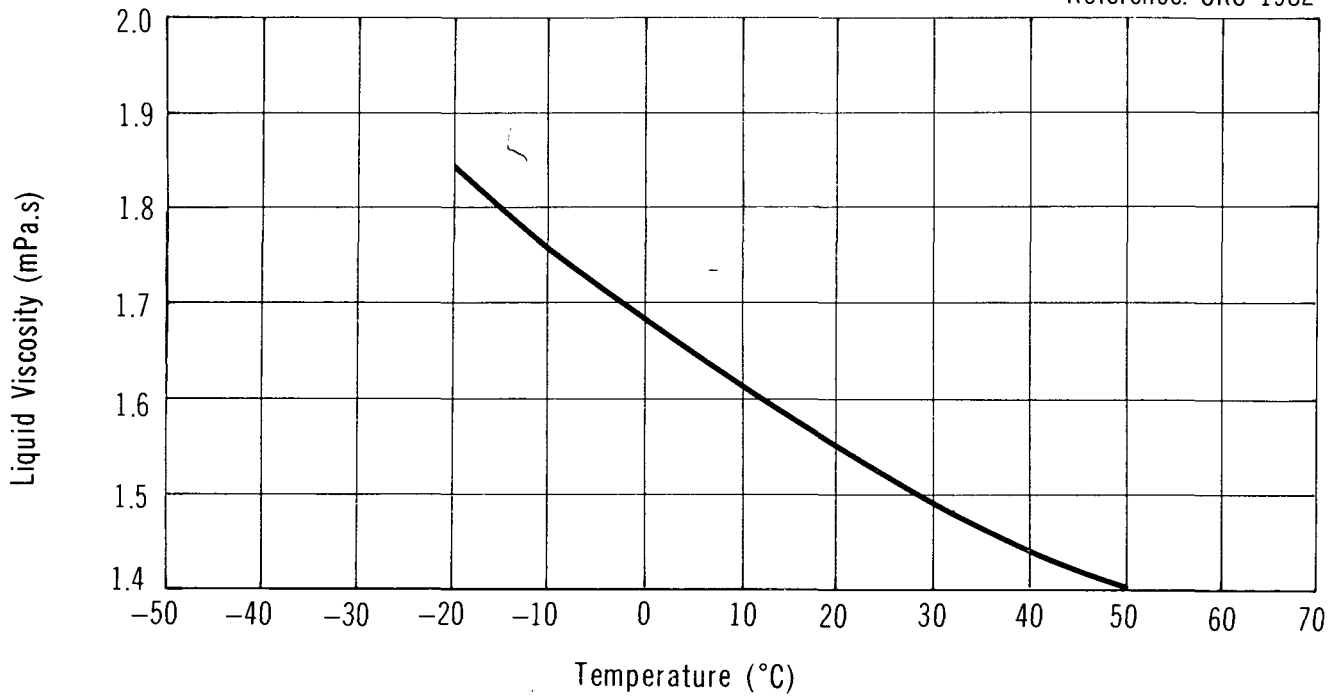
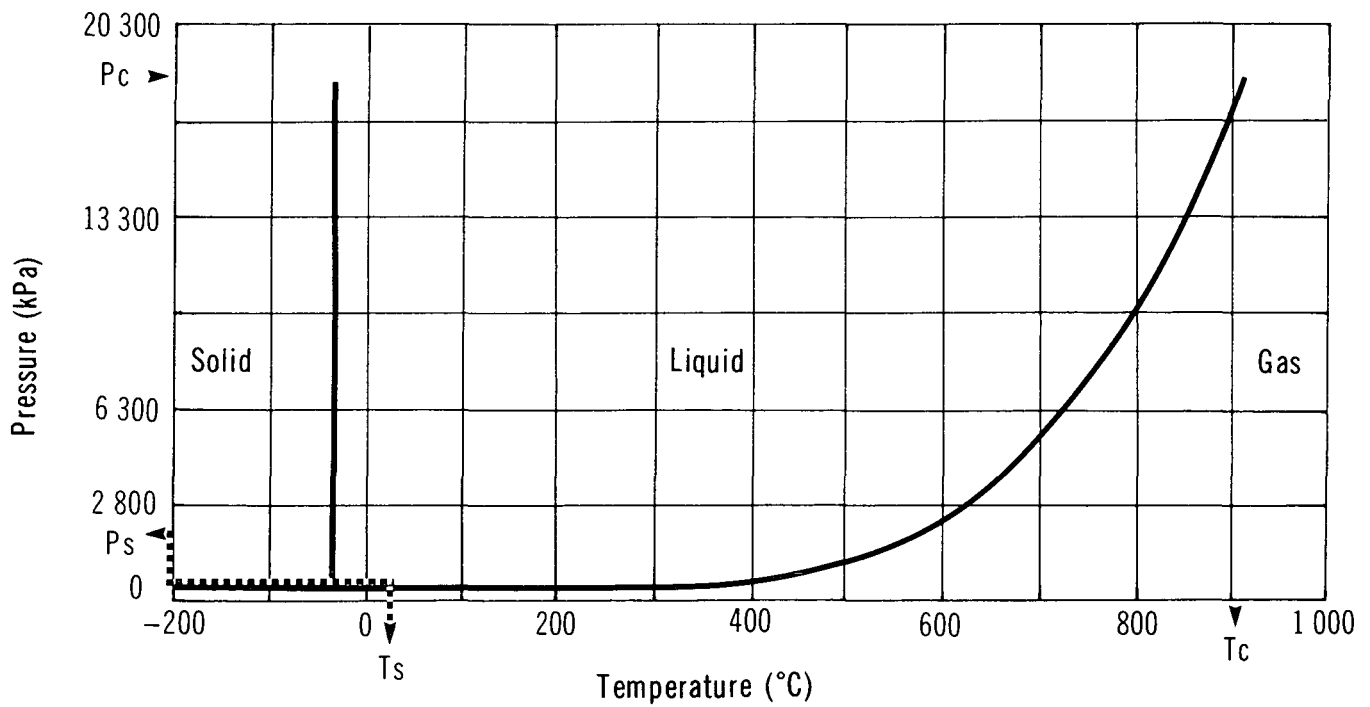


FIGURE 4

MERCURY

PHASE DIAGRAM

3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (CBG 1980)

Mercury is sold in five different grades: commercial (virgin), instrument, redistilled, technical and triple distilled.

3.2 Domestic Manufacturers (CMR 1979)

There are no producers of mercury in Canada. The last mine, Pinchi Lake Mine of Cominco Ltd. in British Columbia, closed in July 1975.

3.3 Suppliers (CBG 1980)

Mercury is imported to the following Canadian distributors:

A & C American Chemical Ltd.
3010 De Baene Street
St. Laurent, Quebec
H4S 1L2
(514) 336-1493

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

Engelhard Industries of Canada Ltd.
512 King Street East
Toronto, Ontario
M5A 1M2
(416) 362-3211

International Chemical Canada Ltd.
P.O. Box 385
Brampton, Ontario
L6V 2L3
(416) 453-4234

Johnson Matthey Limited
Chemical Division
130 Gliddon Road
Brampton, Ontario
L6W 3M8
(416) 453-6120

Philipp Brothers (Canada) Ltd.
1245 Sherbrooke Street West
Montreal, Quebec
H3G 1G9
(514) 845-4294

Van Waters & Rogers Ltd.
9800 Van Horne Way
Richmond, British Columbia
V6X 1W5
(604) 273-1441

3.4 Major Transportation Routes

Mercury is imported and shipped to users throughout Canada.

3.5 Production Levels (CMR 1979; Kirk-Othmer 1981)

Mercury is no longer produced in Canada. Approximately 51 tonnes of mercury were imported in 1979. The metal is produced from ores by standard methods throughout the world. Since the method can be briefly described, it is thought to be a worthwhile and consistent inclusion for this manual. The primary process involves heating

the ore to liberate the metal as vapour which is then cooled in a condensing system to form the liquid. Retorts or furnaces are used for smaller operations; continuous rotary kilns or multiple-hearth furnaces with mechanical feeding and discharge devices are used for larger operations. Recovery efficiency is usually greater than 95 percent, yielding a commercial-grade mercury of 99.9 percent purity. The latter is called prime or commercial virgin mercury. Other methods of recovery of mercury from ore exist but are not of commercial importance at present.

Secondary recovery is afforded from scrap material and industrial and municipal wastes and sludges that contain mercury. Scrap products are first broken down to liberate metallic mercury or its compounds. The metal is then vaporized and condensed to a high purity material. The wastes and sludges are usually treated chemically before roasting.

3.6 Major Uses in Canada (CMR 1979)

Mercury is used in the manufacture of electrical apparatus and in the electrolytic production of chlorine and caustic soda. Electrical uses include mercury lamps, batteries, rectifier bulbs, oscillators and various kinds of switches. It is also used in mildew-proofing paints, in industrial and control instruments, in pesticides, catalysts, and dental preparations, and as a shield against atomic radiation.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Packaging. Prior to shipment, mercury must be packaged as follows (HMR 1978; Keller 1983):

- Glass, earthenware or inner plastic packaging of maximum 2.3 kg (5 lb.) capacity. Each packed in strong outside container. Inside or outside packaging must have completely enveloping inner linings or bags of strong, leak-tight and puncture-resistant materials impervious to mercury.
- Steel or iron flasks in outside packagings. Again, either the inside or outside packaging must have completely enveloping inner linings or bags of strong, leak-tight, and puncture-resistant material impervious to mercury. These flasks typically contain 34.5 kg (76 lb.) of mercury (Kirk-Othmer 1981).

In addition to the above packagings, manufactured devices of which mercury is a component part must be packed in outside packagings having completely enveloping inner linings or bags similar to those previously described.

Devices such as electron tubes and vapour tubes which contain mercury should be packaged in the following manner (HMR 1978; Keller 1983):

- Outside packaging with all seams and joints sealed with self-adhesive, pressure-sensitive tape which will prevent the escape of mercury from outside packages. This type of packaging is applicable only to items containing 454 g (1 lb.) or less of mercury.
- In outside packaging having completely enveloping linings or bags of strong, leak-proof, and puncture-resistant material impervious to mercury.
- In manufacturer's original packaging if tubes are completely jacketed in sealed leak-tight metal cases.
- In manufacturer's original packaging if each item does not contain more than 5 g (0.18 oz.) of mercury per tube and if total net quantity of 30 g (1.1 oz.) or less is contained in the outside package (TDGC 1980).

4.1.2 Bulk Shipment. Mercury is not shipped bulk in railway tank cars, tank motor vehicles or portable tanks. Packages may, of course, be shipped by rail, truck, ship or air.

4.2 Off-loading

Packages containing mercury must be carefully off-loaded in such a manner as to not damage the outer packaging or cause the inner packaging to rupture.

Containers should be stored in a dry, room-temperature environment and must be set in an upright position in accordance with markings on outside packaging.

4.3 Compatibility with Materials of Construction

The compatibility of mercury with materials of construction is indicated in Table 2. Table 3 describes the unbracketed abbreviations. 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 2 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Conditions Temp. (°C)	Material of Construction		
		Recommended	Conditional	Not Recommended
1. Pipes and Fittings	60	PVC I (DPPED 1967)	PVC II (DPPED 1967)	
	66	PP PVDC (DCRG 1978)		
	121	Chlorinated Polyether (DCRG 1978)		
	135	PVDF (DCRG 1978)		
	To operating limit of material	PVC I ABS PE (MWPP 1978)		
2. Valves	49	SS 316 (JSSV 1979)		
3. Others	20	SS 302 SS 304 SS 316 SS 430 (ASS)	SS 410 (ASS)	
	25 (R.T.)	Ti (FMT) Ta (AMC) SS 304, 304L, 316L, 321, 347 Ni, Monel, Inconel (GAC; SFC 1981)		Cu, Cu Alloys (CE 1980b) AL (RLM 1984; CE 1980a)

TABLE 2 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Conditions Temp. (°C)	Material of Construction		
		Recommended	Conditional	Not Recommended
3. Others (Cont'd)	60	PE, PP, POM, NR, NBR, IIR, EPDM, CR, FPM CSM (GF) PVC (TPS 1978)	uPVC (GF) Tufflex, Gatron, Polyester Elastomer, Nylon (CE 1980a)	
	66	PP (TPS 1978)		
	85	CPVC (TPS 1978)		
	121	PVDF (TPS 1978) SBR (GPP)		
	24-316	Glass (CDS 1967)		
	24	Concrete (CDS 1967)		
	24-100	Wood (CDS 1967)		

TABLE 3 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
AL	Aluminum
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene)
CSM	Chlorosulphonated Polyethylene (Hypalon)
Cu	Copper
	Earthenware
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Gatron
	Glass

TABLE 3 MATERIALS OF CONSTRUCTION (Cont'd)

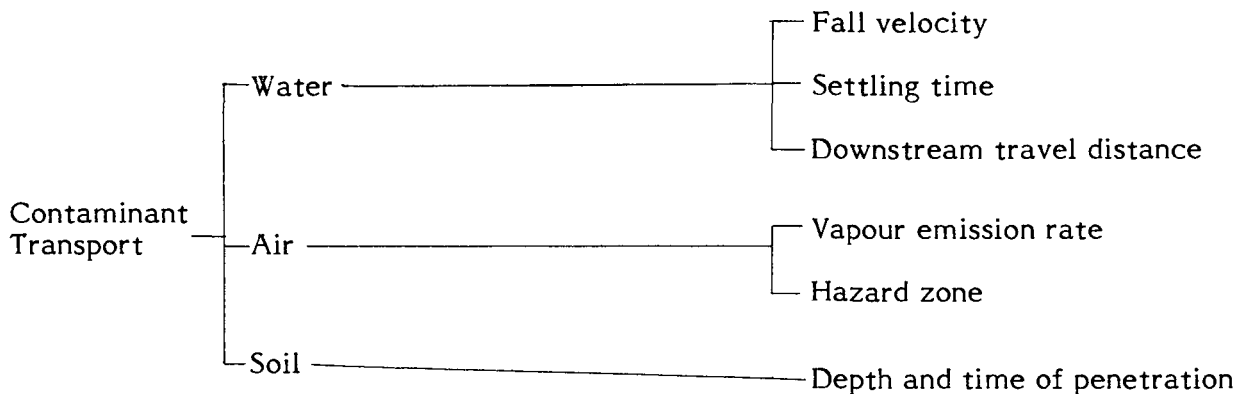
Abbreviation	Material of Construction
	Inconel
	Iron
IIR	Isobutylene/Isoprene (Butyl) Rubber
	Monel
	Nickel
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NBR mod	Buna modification (Neoprene-like)
NR	Natural Rubber
	Nylon
	Polyester
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (followed by grade, if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
SS (followed by grade)	Stainless Steel
Ta	Tantalum
Ti	Titanium
	Tufflex
uPVC	Unplasticized Polyvinyl Chloride
	Wood

5 CONTAMINANT TRANSPORT

5.1 General Summary

Mercury is commonly transported in small containers weighing less than 35 kg. When spilled in water, mercury will sink and spread on the streambed. When spilled on soil, the liquid will spread on the surface and penetrate at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may cause environmental problems. Mercury is fairly volatile; as a result, the vapour released from a liquid pool on the ground surface is a potential environmental hazard.

The following factors are considered for the transport of a spill in water and soil:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. 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

Mercury is commonly shipped in small packages or containers. Consequently, no leak nomograms have been prepared.

5.3 Dispersion in the Air

5.3.1 Introduction. Since mercury is a fairly volatile liquid, vapour released from a liquid pool spilled on a ground surface may constitute a significant hazard downwind. Due to the toxicity of mercury vapour (TLV* = 5×10^{-5} g/m³), an estimation of the hazard distance as a result of a specified spill of mercury on a flat ground surface will be presented.

An evaporation rate for mercury has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for mercury at 30°C and a wind speed of 4.5 m/s (16.1 km/h) is 2×10^{-4} g/(m²·s). For the purposes of this example, a 1 tonne (73.5 L) spill quantity has been chosen and represents a likely upper limit quantity. The spilled mercury is arbitrarily assumed to form a symmetrical pool 2 mm in depth. One tonne will therefore form a pool with a radius of 3.4 m (an area of 36 m²).

The calculated mercury vapour emission rate for the 1 tonne spill is 7.3×10^{-3} g/s. Under weather condition F, for a mercury hazard concentration of 10 times the TLV* (or 5×10^{-4} g/m³), the estimated maximum downwind hazard distance is much less than 100 m. Since the example represents a likely worst case situation, the example spill and spills of mercury at lower temperatures and/or involving lesser spill quantities may be treated by arbitrarily assigning a hazard distance of 100 m from the pool in all directions.

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, mercury sinks and spreads on the stream bottom. Nomograms have been prepared to estimate the length of the zone of contamination in a non-tidal river. This represents the worst case scenario for the extent of the zone of contamination.

To estimate the extent of the downstream contamination on a river bed resulting from a spill of an insoluble, high density liquid in water, the terminal fall velocities (V_t) of the discrete particles have been estimated using a mathematical model (Thibodeaux 1979). The fall velocity of an individual particle is a function of its specific gravity, size and cross-sectional area, together with the density and viscosity of water. The drag force, tending to resist fall of the particle through water, varies for different flow regimes. Details of the model are outlined in the Introduction Manual.

5.4.2 Nomograms. The following nomograms are presented to estimate the extent of the downstream zone of contamination on a river bed following a spill of mercury.

Figure 5: terminal fall velocity versus particle diameter

Figure 6: settling time versus terminal fall velocity for a range of stream depths

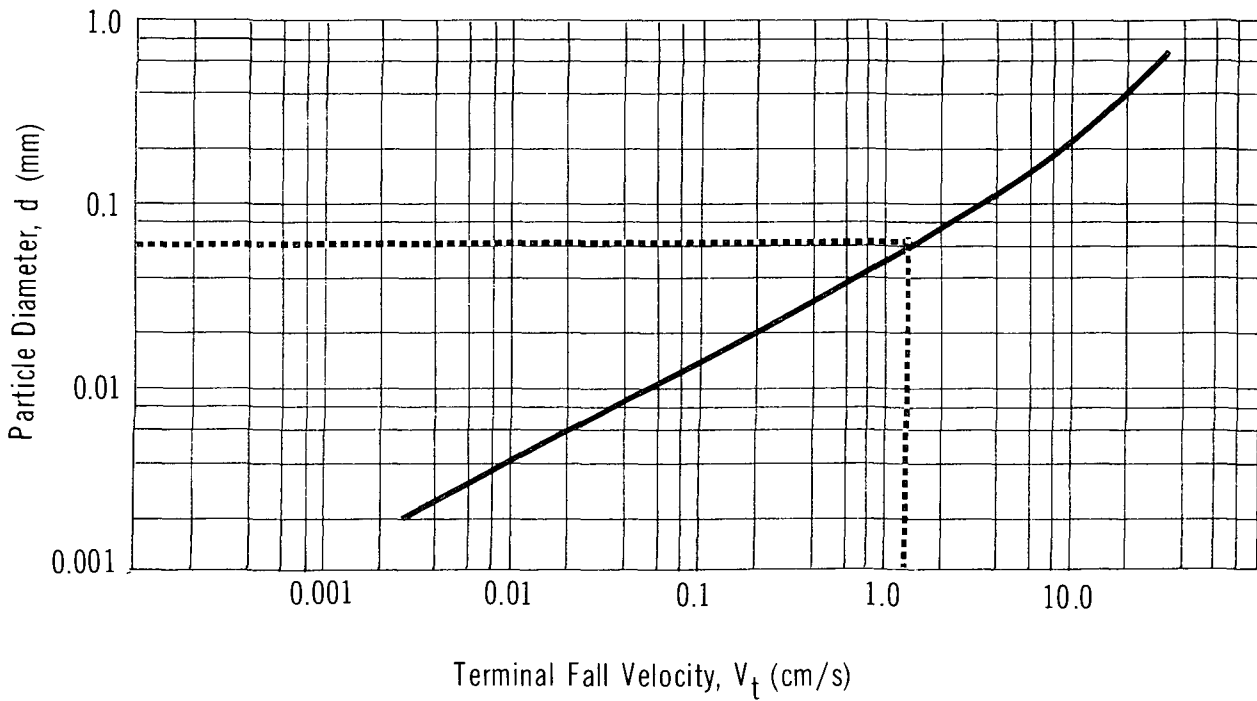
Figure 7: downstream distance versus settling time for a range of average stream velocities

5.4.2.1 Figure 5: Terminal fall velocity versus particle diameter. The terminal fall velocity (V_t) of discrete particles of mercury in water can be estimated from Figure 5 for a given equivalent particle diameter.

FIGURE 5

MERCURY

TERMINAL FALL VELOCITY vs PARTICLE DIAMETER



5.4.2.2 Figure 6: Settling time versus terminal fall velocity. For a given particle size, the terminal fall velocity (V_t), the time (t) to settle to the bottom of a river of depth (d), neglecting any turbulent mixing effects, can be estimated from Figure 6.

5.4.2.3 Figure 7: Downstream distance versus settling time. Based on the settling time derived from Figure 6, the downstream distance (X) at which the given particle size will reach the river bed can be determined from Figure 7 for a range of average stream velocities.

5.4.3 Sample Calculation. A 1 tonne spill of mercury has occurred in a river. The stream depth is 5 m and the average stream velocity is 1 m/s. How far downstream will a discrete particle 0.06 mm in diameter be carried before reaching the streambed? Neglect the effect of stream turbulence.

Solution

Step 1: Define terminal fall velocity (V_t)

- . Use Figure 5
- . With $d = 0.06$ mm, $V_t = 1.2$ cm/s

Step 2: Determine time for particle to settle to river bed

- . Use Figure 6
- . With $V_t = 1.2$ cm/s, and for a stream depth of 5 m, the settling time is 7 min

Step 3: Determine downstream distance

- . Use Figure 7
- . With $t = 7$ min and stream velocity (U) = 1 m/s, the downstream travel distance (X) of a particle 0.06 mm in diameter is 300 m

5.5 Subsurface Behaviour: Penetration into Soil

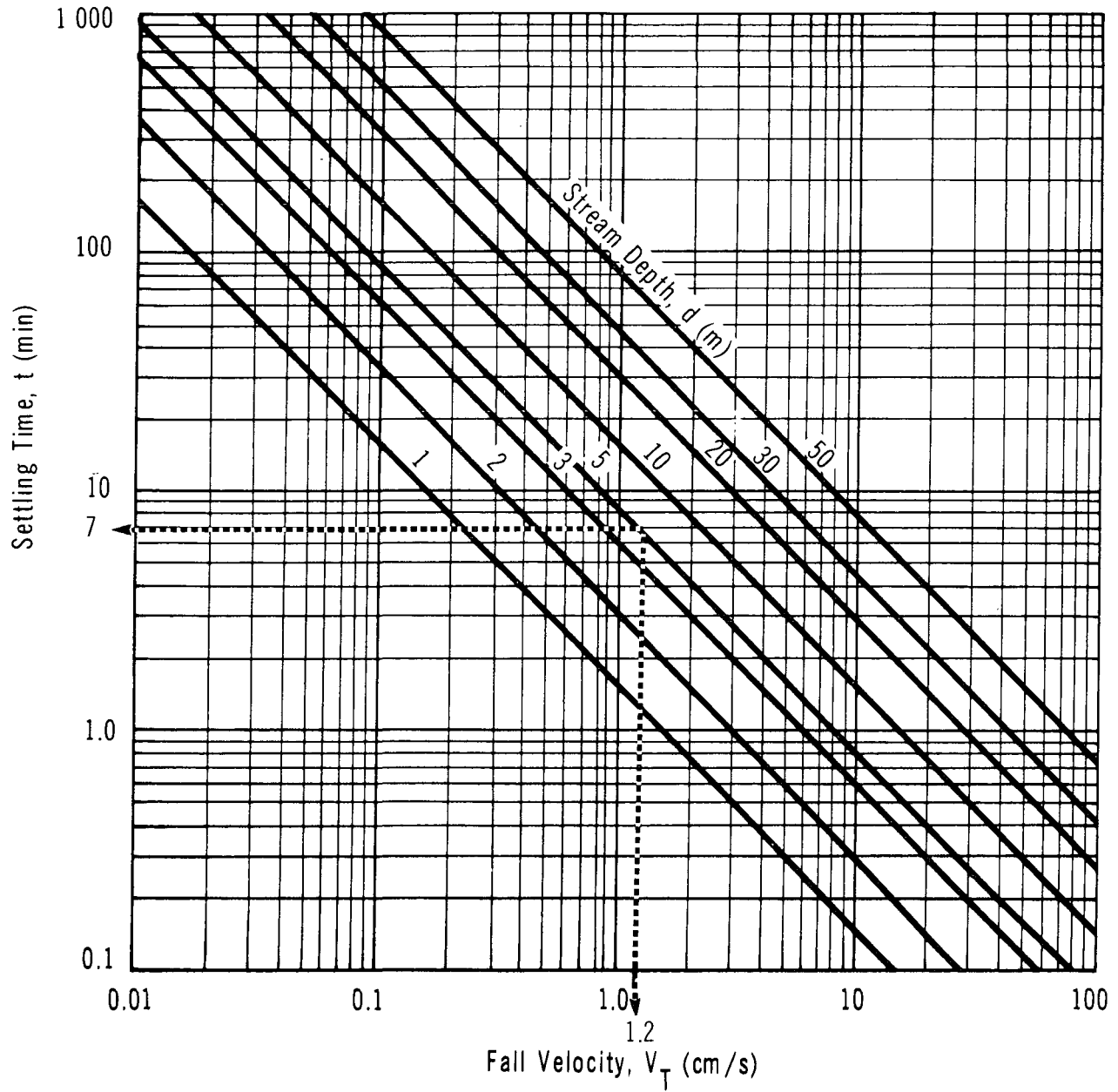
5.5.1 Introduction. The general principles of contaminant transport in soil and their application to this work are described in the Introduction Manual. Specific items related to mercury and the development of nomograms for it are presented below.

Mercury has a very low solubility in water. Consequently, when spilled onto soil, its infiltration and transport downward through the soil involve multi-media phenomena. The media of concern are mercury, water, soil, and vapours of mercury.

Unfortunately, sufficient data do not exist to permit a detailed assessment of mercury transport in a specific circumstance. A few extensive field investigations have

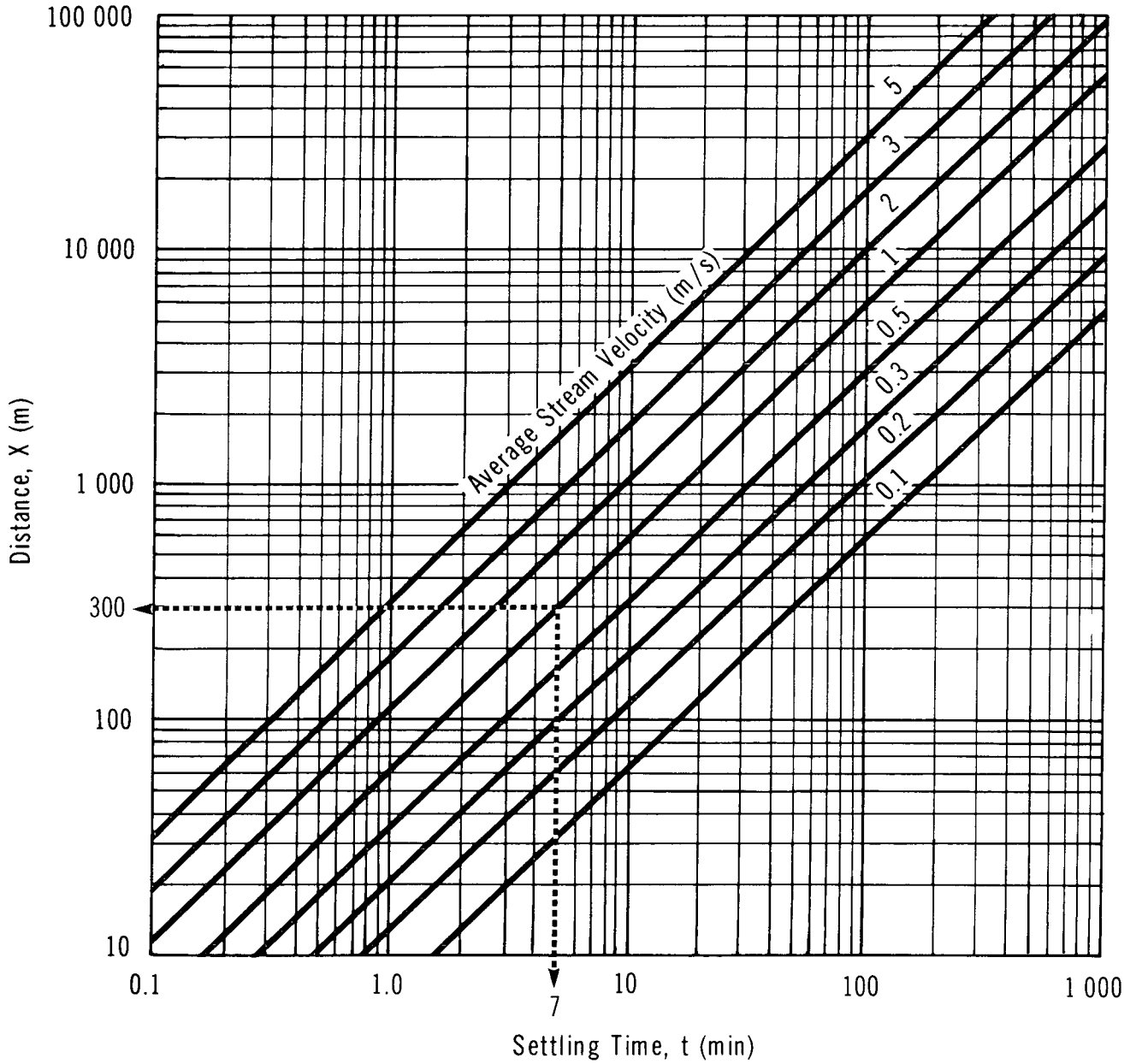
MERCURY

SETTLING TIME vs FALL VELOCITY



MERCURY

DOWNSTREAM DISTANCE vs SETTLING TIME



been carried out, especially involving spills of oil, gasoline and PCBs. However, very limited information exists for mercury. Consequently, it is necessary to simplify the soil and groundwater conditions and to express contaminant behaviour through analogy to other more extensively studied materials. A pattern for the downward movement of immiscible fluids in soil has been prepared by comparison to oil spilled onto soil surfaces (Blokker 1971; Freeze and Cherry 1979).

It is assumed that when the spill occurs, the soil contains water only up to its field capacity and that this condition prevails down to the groundwater table. The spilled mercury fills the pores at the soil surface and begins to penetrate downward. It is assumed that mercury moves downward through the soil as a saturated slug. Some lateral spreading may occur due to capillary action. Since mercury is much denser than water, it will continue to move downward upon reaching the groundwater table. This is shown schematically in Figure 8.

5.5.2 Equations Describing Mercury Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Mercury in Soil. The saturated hydraulic conductivity (K_0), in m/s, is given by:

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

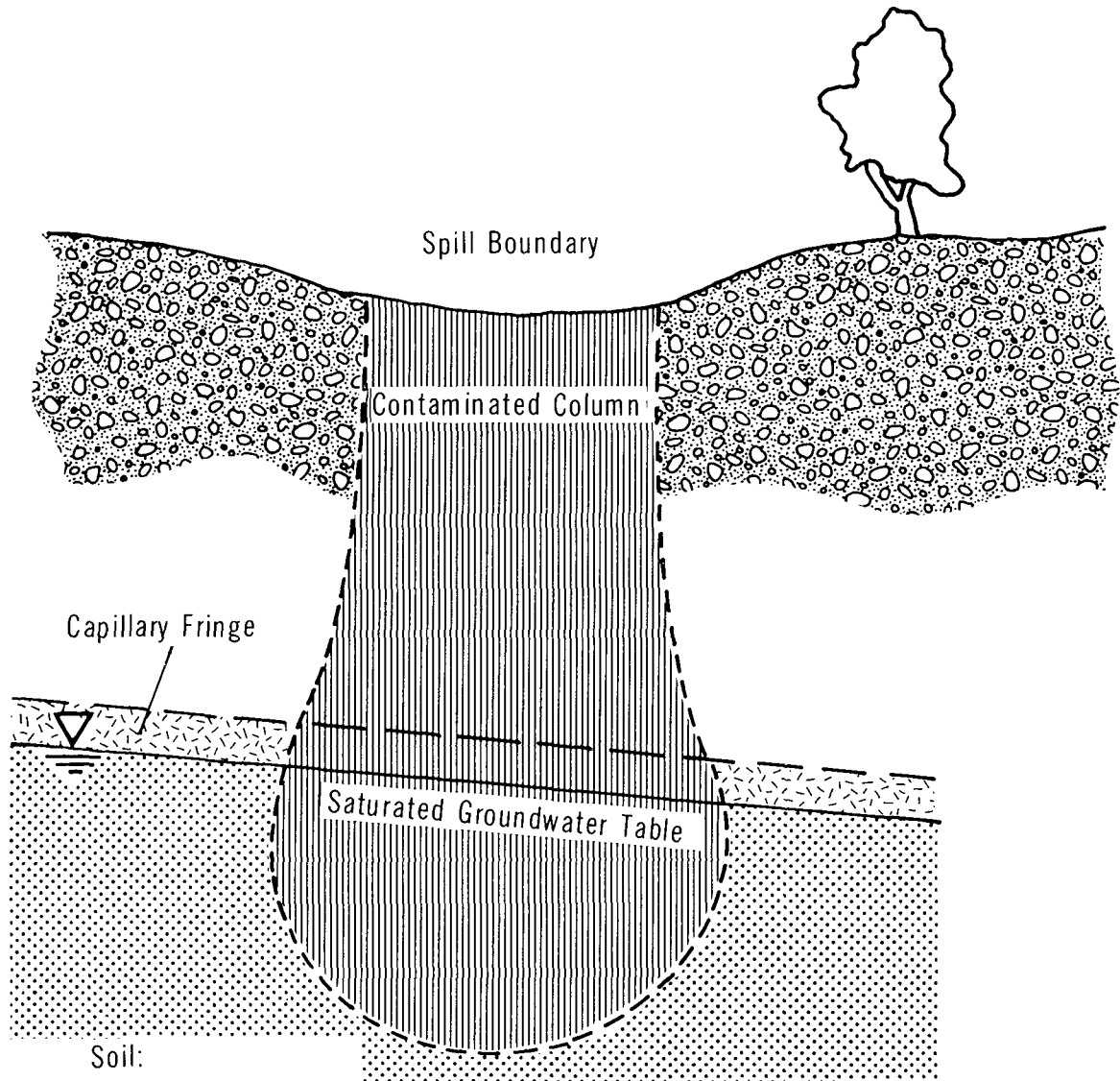
where: k = intrinsic permeability of the soil (m^2)
 ρ = mass density of the fluid (kg/m^3)
 μ = absolute viscosity of the fluid ($Pa \cdot s$)
 g = acceleration due to gravity = $9.81 m/s^2$

The appropriate properties of mercury are given in the chart below:

Property	Mercury	
	20°C	4°C
Mass density (ρ), kg/m^3	13 522	13 536
Absolute viscosity (μ), $Pa \cdot s$	1.54×10^{-3}	1.65×10^{-3}
Saturated hydraulic conductivity (K_0), m/s	$(8.6 \times 10^7)k$	$(8.0 \times 10^7)k$

MERCURY

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. The Introduction Manual describes the three soils 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 mercury 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 9. The nomograms are presented as Figures 10, 11 and 12.

5.5.6 Sample Calculation. A 1 tonne spill of mercury has occurred on silty sand. The temperature is 20°C. The spill radius is 3.4 m. Calculate the depth of penetration 12 hours after the spill.

Solution

Step 1: Define parameters

- Mass spilled = 1000 kg (1 tonne)
- $T = 20^\circ\text{C}$
- $r = 3.4$ m
- Soil = silty sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 12 h

Step 2: Calculate area of spill

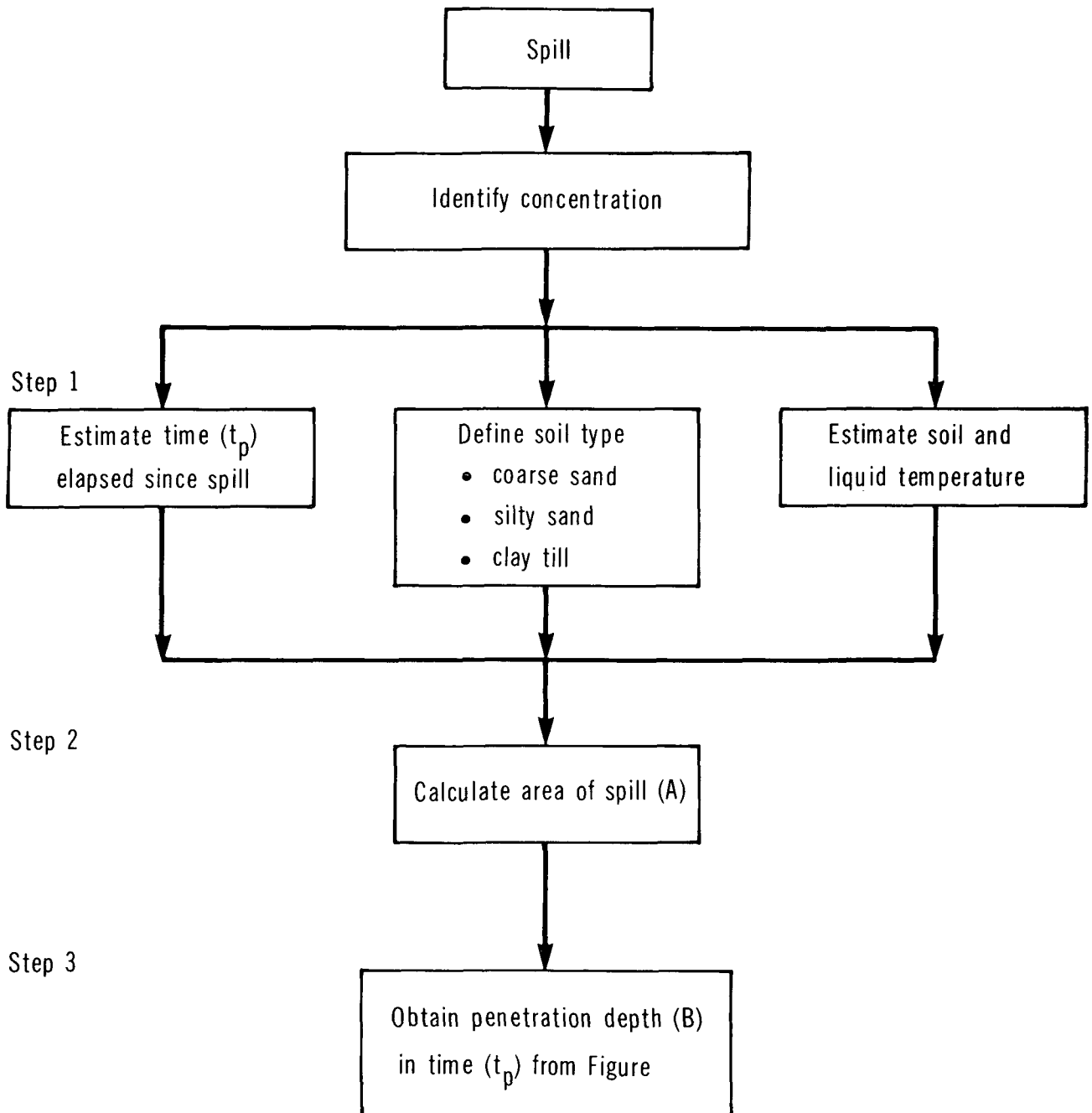
- $A = \pi r^2 = 36$ m²

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

- For silty sand, $B = 3.6$ m at $t_p = 12$ h = 0.5 d
- Groundwater table has not been reached in this time

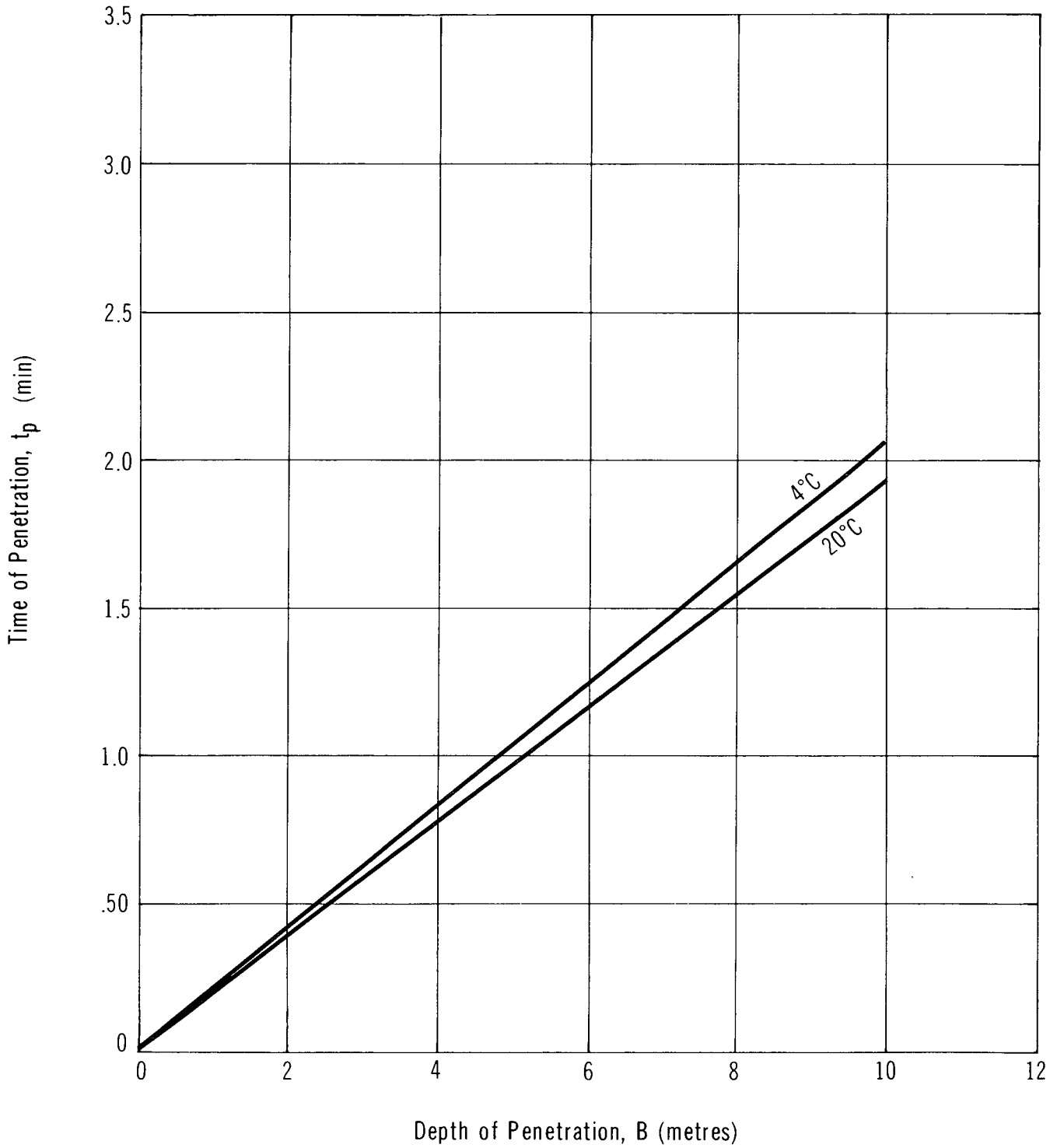
MERCURY

FLOWCHART FOR NOMOGRAM USE



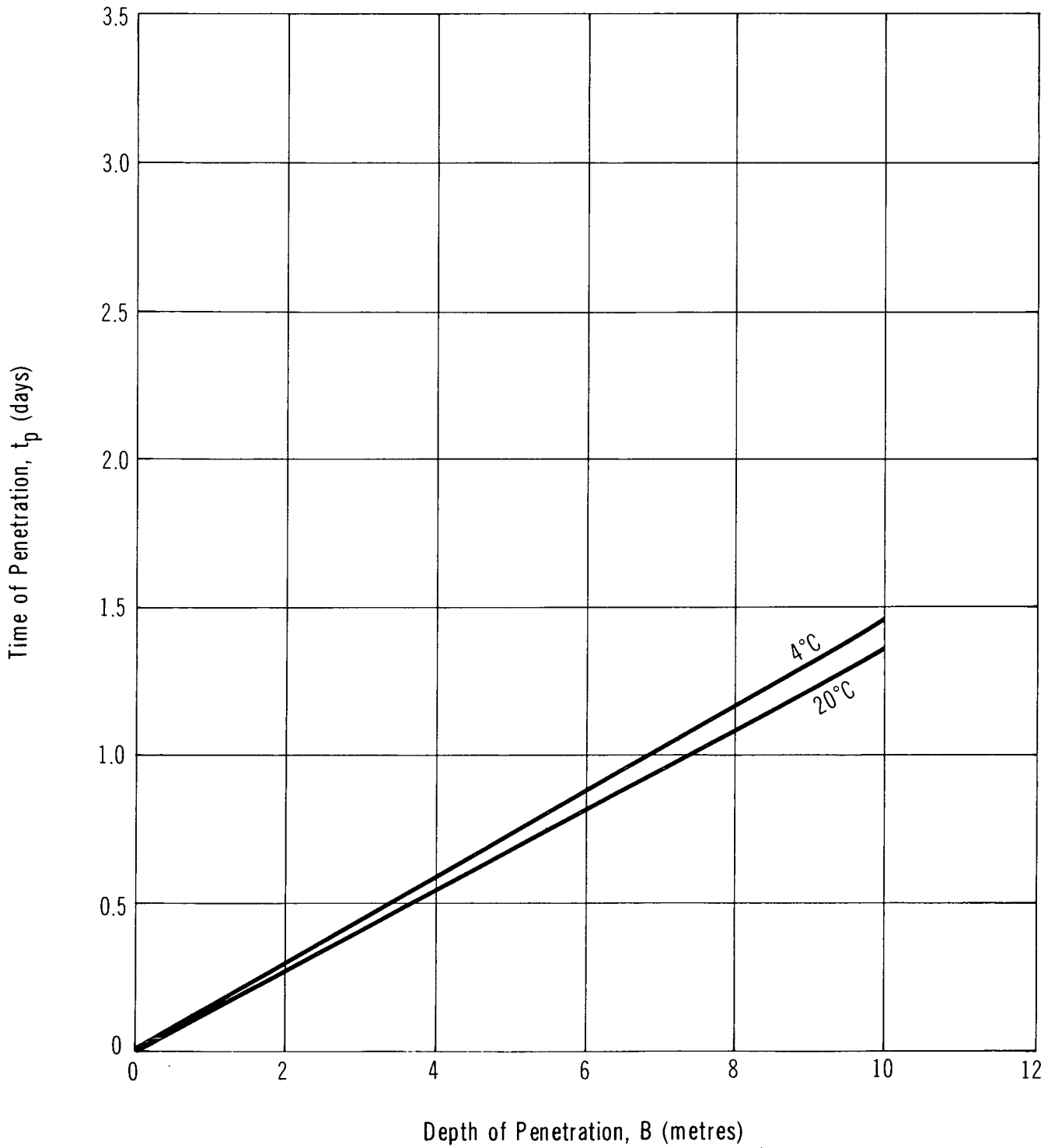
MERCURY

PENETRATION IN COARSE SAND



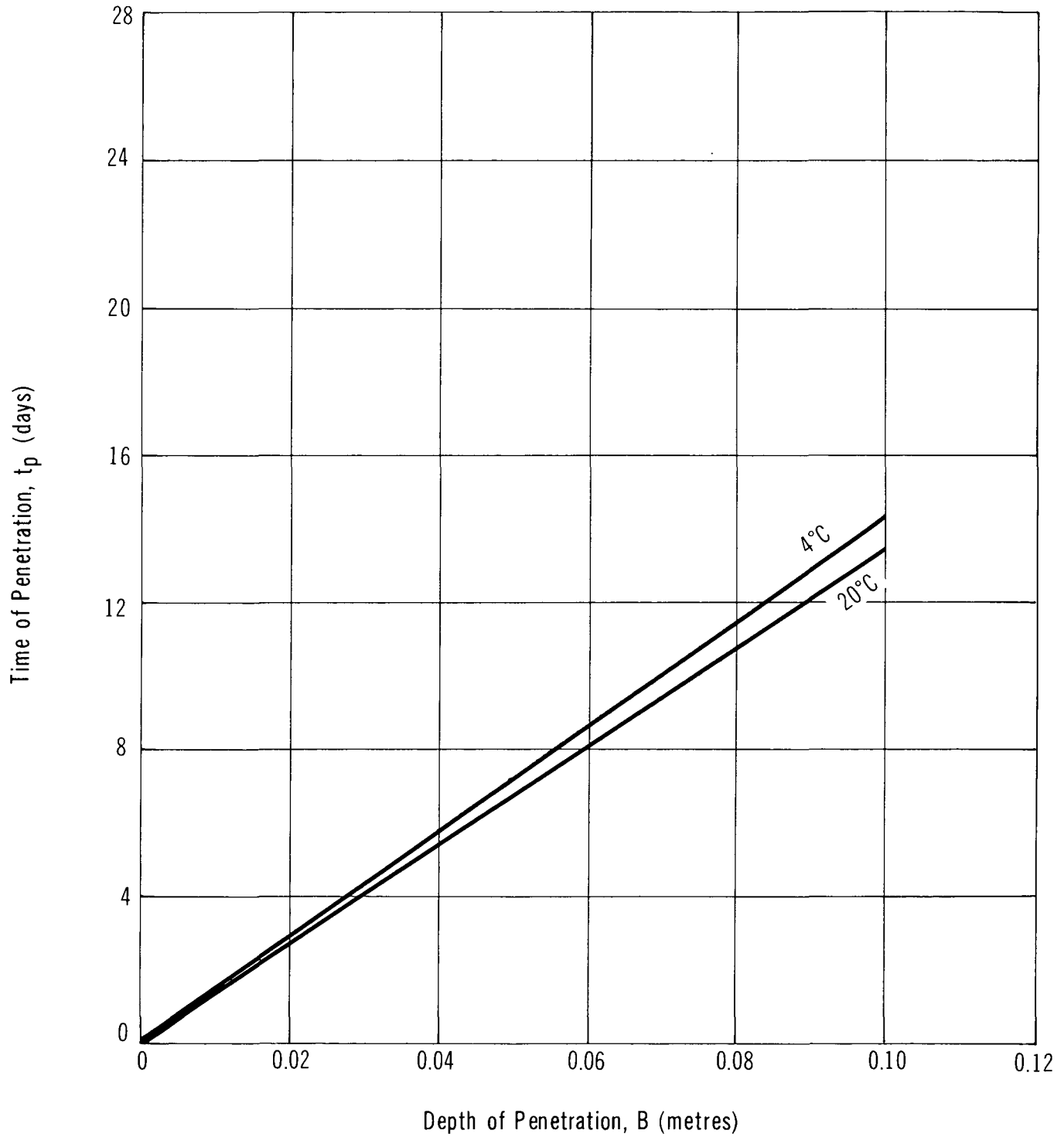
MERCURY

PENETRATION IN SILTY SAND



MERCURY

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Health and Welfare Canada recommends 0.001 mg/L mercury as a maximum acceptable concentration for drinking water, with an objective of 0.0002 mg/L. Ontario has adopted the same objective for livestock watering and has a criterion of 0.01 mg/L (Guidelines/Canadian/Water 1978; Water Management Goals 1978).

6.1.2 Air. The Ontario limit for airborne environmental mercury is 5 $\mu\text{g}/\text{m}^3$ (free and combined, max. 0.5 h) (Ontario E.P. Act 1971; EPS 1979). The ambient air quality standard for mercury under the same act is 2.0 $\mu\text{g}/\text{m}^3$ over 24 hours (EPS 1979).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. No $\text{TL}_{\text{m}} 96$ has been assigned to elemental mercury; for those mercury compounds that have been assigned ratings, they are generally from 10 to 1 mg/L or less than 1 mg/L; for example, the value for mercury (II) chloride is <1 ppm (RTECS 1979).

The lack of a sufficient data base for the toxicity of inorganic mercury to freshwater aquatic life is the reason no guidelines have been established. Based primarily on saltwater toxicity data, the U.S. EPA has recommended a limit (24-h average) of 0.064 $\mu\text{g}/\text{L}$ of inorganic mercury for the protection of freshwater aquatic life. The maximum concentration should not exceed 3.2 $\mu\text{g}/\text{L}$ at any time. Based on guideline data, the criterion for methylmercury is 0.016 $\mu\text{g}/\text{L}$ as a 24-h average; the concentration should not exceed 8.8 $\mu\text{g}/\text{L}$ at any time. For saltwater aquatic life, the criterion for inorganic mercury is 0.19 $\mu\text{g}/\text{L}$ as a 24-h average; the concentration should not exceed 1.0 $\mu\text{g}/\text{L}$ at any time. These saltwater data were derived from the guidelines. The methylmercury criterion for saltwater aquatic life was derived from freshwater data and is set at 0.025 $\mu\text{g}/\text{L}$ as a 24-h average; the concentration should not exceed 2.6 $\mu\text{g}/\text{L}$ at any time (PTP 1980).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Fish Kill Data</u>					
1 to 5	24	Fish (<i>T. mossambica</i>)	fatal	pH 7.5, 28°C	Panigrahi 1980
1.0 (in- organic Hg)	96	Fish	fatal	bioassay	WQC 1972
0.0002 (dimethyl Hg)	6 wk	Fathead minnows	killed		WQC 1972
5	10	Goldfish	lethal		Haga 1970
0.01	6	Stickleback	lethal	15 to 18°C	Klein 1957
0.0	2 wk	Japanese medaka, juvenile (1 wk old)	mortality rate = 2.2%	control fish	Chan 1978
4.3 µg/L	2 wk	Japanese medaka, juvenile (1 wk old)	mortality rate = 54.3%	as CH ₃ Hg ⁺	Chan 1978
10.7 µg/L	2 wk	Japanese medaka, juvenile (1 wk old)	mortality rate = 64.9%	as CH ₃ Hg ⁺	Chan 1978
21.5 µg/L	2 wk	Japanese medaka, juvenile (1 wk old)	mortality rate = 99.4%	as CH ₃ Hg ⁺	Chan 1978
0	10 d	Japanese medaka, eggs	mortality rate = 7%	control, 21°C	Dial 1978
40 µg/L	10 d	Japanese medaka, eggs	mortality rate = 5%	as CH ₃ HgCl, 21°C	Dial 1978
60 µg/L	10 d	Japanese medaka, eggs	mortality rate = 15%	as CH ₃ HgCl, 21°C	Dial 1978
80 µg/L	10 d	Japanese medaka, eggs	mortality rate = 45%	as CH ₃ HgCl, 21°C	Dial 1978
5-15 µg/L	24	<i>Anabas scandens</i>	100% mortality (40 fish)	as Hg(NO ₃) ₂	Panigrahi 1978

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.01	not stated	Guppy	killed	designated as Hg static bioassay, acute	WQC 1971
0.008	10 d	Stickleback, 3-spine	survival time	as HgCl ₂ , static bioassay, acute, pH 6.0-6.8, 15-18°C	WQC 1971; Jones 1969
0.003 N	14 min	Stickleback, 12-spine	survival time	as HgCl ₂ , continuous flow, bioassay	WQC 1971; Jones 1969
0.002 N	22 min	Stickleback, 12-spine	survival time	as HgCl ₂ , continuous flow, bioassay	WQC 1971; Jones 1969
0.0003 N	31 min	Stickleback, 12-spine	survival time	as HgCl ₂ , continuous flow, bioassay	WQC 1971; Jones 1969
0.00004 N	100 min	Stickleback, 12-spine	survival time	as HgCl ₂ , continuous flow, bioassay	WQC 1971; Jones 1969
0.80 and 0.41 µg/L	3 mo	Fathead minnow	100% mortality rate	CH ₃ HgCl	QCW 1976
0.23 µg/L	3 mo	Fathead minnow	92% mortality rate	CH ₃ HgCl	QCW 1976
0.12 µg/L	3 mo	Fathead minnow	spawning completely inhibited and males did not develop sexually	CH ₃ HgCl	QCW 1976
0.07 µg/L	Duration, full life cycle test	Fathead minnow	no toxic effects noted on survival	CH ₃ HgCl	QCW 1976

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
			or growth of off- spring		
0.2	4 d	Stickleback, 3-spine	survival time	HgCl ₂ , static bio- assay, acute, pH 6.0-6.8, 15-18°C	Jones 1969
0.4	2.5 d	Stickleback, 3-spine	survival time	HgCl ₂ , static bio- assay, acute, pH 6.0-6.8, 15-18°C	Jones 1969
0.8	17 d	Stickleback, 3-spine	survival time	HgCl ₂ , static bio- assay, acute, pH 6.0-6.8, 15-18°C	Jones 1969
2.0	5 d	Stickleback, 3-spine	survival time	HgCl ₂ , static bio- assay, acute, pH 6.0-6.8, 15-18°C	Jones 1969
4	100 min	Stickleback, 3-spine	survival time	HgCl ₂ , static bio- assay, acute, pH 6.0-6.8, 15-18°C	Jones 1969
0.01 (Hg)	204	Rainbow trout	lethal limit	HgCl ₂ , 15-23°C	Jones 1969
0.15 (Hg)	108	Rainbow trout	lethal limit	HgCl ₂ , 15-23°C	Jones 1969
1.0 (Hg)	600	Rainbow trout	lethal limit	HgCl ₂ , 15-23°C	Jones 1969
<u>Fish Toxicity Tests</u>					
0.240 (HgCl ₂)	96	Coho salmon, juvenile	LC ₅₀ ^{1,2}	R, M ³	AWQC 1983
0.275 (HgCl ₂)	96	Rainbow trout, juvenile	LC ₅₀ ^{1,2}	FT, M	AWQC 1983
0.1587 (HgCl ₂)	96	Fathead minnow	LC ₅₀ ^{1,2}	FT, M	AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.180 (HgCl ₂)	96	Mosquitofish, female	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.030 (HgCl ₂)	96	Guppy (116-157 mg)	LC ₅₀ ¹	R, U	AWQC 1983
0.04025 (HgCl ₂)	96	Guppy (363-621 mg)	LC ₅₀ ^{1,2}	R, U	AWQC 1983
0.160 (HgCl ₂)	96	Bluegill, juvenile	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.024 (CH ₃ HgCl)	96	Rainbow trout, larva	LC ₅₀ ¹	R, U	AWQC 1983
0.042 (CH ₃ HgCl)	96	Rainbow trout, juvenile	LC ₅₀ ¹	R, U	AWQC 1983
0.025 (CH ₃ HgCl)	96	Rainbow trout, juvenile	LC ₅₀ ¹	FT, U	AWQC 1983
0.02789 (CH ₃ HgCl)	96	Rainbow trout, juvenile	LC ₅₀ ^{1,2}	FT, M	AWQC 1983
0.07389 (CH ₃ HgCl)	96	Brook trout, yearling, juvenile	LC ₅₀ ^{1,2}	FT, M	AWQC 1983
0.35	96	Catfish	LC ₅₀		Spehar 1981
0.088 ± 0.098 (CH ₃ Hg ⁺)	96	Japanese medaka	LC ₅₀	S, BA	Chan 1978
0.13	96	Pumpkinseed	LC ₅₀		EPA 440/9-75-009
0.3	96	Carp	LC ₅₀		WQC 1972
0.23	96	Mummichog (killifish)	LC ₅₀	20 to 22°C	WQC 1972
0.5 to 1	48	Goldfish	TL _m		EPA 440/9-75-009
0.140 (HgSO ₄)	168	Pink salmon, larva	LC ₅₀		AWQC 1983
0.290 (HgSO ₄)	168	Sockeye salmon, larva	LC ₅₀		AWQC 1983
0.190 (HgSO ₄)	168	Sockeye salmon, juvenile	LC ₅₀		AWQC 1983
0.903 (HgCl ₂)	24	Rainbow trout, juvenile	LC ₅₀		AWQC 1983
0.500 (HgCl ₂)	10 d	Mosquitofish	LC ₅₀		AWQC 1983
0.013 (HgCl ₂)	24	Guppy	LC ₅₀		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.010 Hg	21 d	Largemouth bass	threshold of effect, opercular rhythm		AWQC 1983
0.500 (CH ₃ HgCl)	<24	Mosquitofish	LC ₅₀		AWQC 1983
0.0085 (HgSO ₄)	2 d	Pink salmon, pre- eyed embryo	LC ₁₀₀		AWQC 1983
0.0093 (HgSO ₄)	2 d	Sockeye salmon, pre- eyed embryo	LC ₁₀₀		AWQC 1983
0.0052 (HgSO ₄)	2 d	Pink salmon, embryo	EC ₃₂ to EC ₈₁	deformity	AWQC 1983
0.0043 (HgSO ₄)	2 d	Sockeye salmon, embryo	EC _{45.6}	deformity	AWQC 1983
0.074 (HgCl ₂)	2	Rainbow trout, juvenile	depressed olfactory bulbar response		AWQC 1983
0.0002 (HgCl ₂)	80 min	Rainbow trout	avoidance threshold		AWQC 1983
0.00012 to 0.00024 (HgCl ₂)	5, 18 mo	Rainbow trout	substantial mortality		AWQC 1983
3.000 (HgCl ₂)	60-72	Common carp, embryo	reduced hatching success		AWQC 1983
0.008 (CH ₃ HgCl)	14 d	Rainbow trout, juvenile	LC ₈₀		AWQC 1983
48 mg/kg in food	120 d	Rainbow trout	loss of appetite	CH ₃ HgCl + inorganic Hg	AWQC 1983
48 mg/kg in food	269 d	Rainbow trout	loss of nervous control	CH ₃ HgCl + inorganic Hg	AWQC 1983
1.000 (CH ₃ HgCl)	30 min	Rainbow trout	EC ₅₀	reduced viability of sperm	AWQC 1983
0.0007 (CH ₃ HgCl)	incuba- tion period + 21 d	Brook trout, alevin	reduced growth		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.00079 (CH ₃ HgCl)	30 d	Brook trout, alevin	increased enzyme (GOT) activity		AWQC 1983
0.00293 (CH ₃ HgCl)	14 d	Brook trout, juvenile	increased blood plasma chloride		AWQC 1983
>0.003 (CH ₃ HgCl)	8 d	Brook trout	increased cough frequency		AWQC 1983
7 µg/g in food	8 d	Rainbow trout	muscle tissue levels reached 10.4 µg/g	CH ₃ HgCl + inorganic Hg	Jacobs 1978. IN EPA 600/J-79-073
1.02 µg/g in food	8 d	Rainbow trout	muscle tissue levels reached 0.67 µg/g	CH ₃ HgCl + inorganic Hg	Jacobs 1978. IN EPA 600/J-79-073
0.050 (HgCl ₂)	1 wk	Rainbow trout	reduced hematocrit and osmo- lality		AWQC 1983
8.000 (HgCl ₂)	36 min	White sucker, adult	blood enzyme (LDH) inhibition 20%		AWQC 1983
10.000 (HgCl ₂)	46 min	White sucker, adult	blood enzyme (GOT) inhibition 20%		AWQC 1983
0.0003 (HgCl ₂)	10 d	Channel catfish, embryo, larva	EC ₅₀ , death and deformity		AWQC 1983
0.0887 (HgCl ₂)	7-8 d	Bluegill, embryo, larva	EC ₅₀ , death and deformity		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.1372 (HgCl ₂)	7-8 d	Redear sunfish, embryo, larva	EC ₅₀ , death and deformity		AWQC 1983
0.0053 (HgCl ₂)	8 d	Largemouth bass, embryo, larva	EC ₅₀ , death and deformity		AWQC 1983
0.010	24	Largemouth bass,	affected opercular rhythm		AWQC 1983
0.310 (Hg(NO ₃) ₂)	35 d	Mozambique tilapia	clinical symptoms		AWQC 1983
0.005 (CH ₃ HgCl)	1 wk	Rainbow trout	reduced hematocrit and osmo- lality		AWQC 1983
0.00088 (CH ₃ HgCl)	16-17 d	Brook trout, embryo	decreased enzyme (GOT) activity		AWQC 1983
27 µg/L (HgCl ₂)	not stated	Brook trout, embryo	signifi- cant re- productive impair- ment		QCW 1976
0.04 µg/L (CH ₃ HgCl)	not stated	Brook trout, embryo	signifi- cant re- productive impair- ment		QCW 1976
43-1000 µg/L		Japanese medaka	tissue level of CH ₃ Hg ⁺ was below 40 µg/g	as CH ₃ Hg ⁺	Chan 1978
<1000 µg/L		Japanese medaka	steadily accumu- lates CH ₃ Hg ⁺ to a high of 408.1 µg/g	as CH ₃ Hg ⁺	Chan 1978

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
8.5 and 42.9 $\mu\text{g/L}$	on alternate days during oviposition period	Japanese medaka	inhibition of oviposition only on exposure days	as CH_3Hg^+	Chan 1978
85 $\mu\text{g/L}$	on alternate days during oviposition period	Japanese medaka	complete inhibition of oviposition on all days	as CH_3Hg^+	Chan 1978
4.3, 10.7 and 21.5 $\mu\text{g/L}$	6 wk	Japanese medaka	inhibition of spawning; both male and female gonads showed reduction in size; females were more sensitive; hatchability of spawned eggs not affected	as CH_3Hg^+	Chan 1978
40 $\mu\text{g/L}$	20 d	Japanese medaka, eggs/young	7 eggs hatched; young swam in an erratic manner (neurological effects)	as CH_3HgCl	Dial 1978
60 $\mu\text{g/L}$	20 d	Japanese medaka, eggs/young	1 egg hatched; very uncoordinated movements	as CH_3HgCl	Dial 1978
80 $\mu\text{g/L}$	20 d	Japanese medaka, eggs	no eggs hatched	as CH_3HgCl	Dial 1978

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
80 µg/L	25 d	Japanese medaka, eggs	no eggs hatched	as CH ₃ HgCl	Dial 1978
40 to 80 µg/L	10-25 d	Japanese medaka, eggs	severity of defects in eggs increased with CH ₃ HgCl concentration	as CH ₃ HgCl	Dial 1978
9 µg/L		Blue gourami (<i>Trichogaster trichopterus</i>)	decrease in immune response to both infectious pancreatic necrosis and to <i>Proteus vulgaris</i>	as CH ₃ HgCl	Roales 1977
3	after 5 d	<i>Anabas scandens</i>	appeared lethargic (35 fish)	as Hg(NO ₃) ₂	Panigrahi 1978
3	after 8 d	<i>Anabas scandens</i>	regained pre-test activity; feeding was normal	as Hg(NO ₃) ₂	Panigrahi 1978
3	after 20 d	<i>Anabas scandens</i>	blindness and exophthalmia noted in 10 fish	as Hg(NO ₃) ₂	Panigrahi 1978
3	after 28 d	<i>Anabas scandens</i>	similar swelling and blindness observed in 10 more fish; all survived, but showed a variety of pathologi-	as Hg(NO ₃) ₂	Panigrahi 1978

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
			cal and biochemical disorders, including blindness (71%)		
3	after 36 d	<i>Anabas scandens</i>	total of 24 fish affected; post-mor- tem show- ed liver was con- gested, pale, ten- der and small com- pared to control fish; RBC count and protein content were less than con- trol fish; hemoglo- bin % was lower	as Hg(NO ₃) ₂	Panigrahi 1978
3	after 45 d	<i>Anabas scandens</i>	residual Hg con- centra- tion was as high as 2.8 + 0.18 µg/g live weight in muscle, 3.0 + 0.16 µg/g live weight in liver	as Hg(NO ₃) ₂	Panigrahi 1978
0.25	1 d	Goldfish	sublethal effects, mercury accumulat-	as HgCl ₂	WQC 1973

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
			ed rapidly up to 0.1 ppm. At high conc., heavy mucus formation occurred, with most of the Hg being found in the mucus. At 0.25 ppm, fish has 15 ppm tissue residue in 1 d and 40-50 ppm tissue residue in 100 h		
0.82	7 d	Goldfish	TL _m	as HgCl ₂	WQC 1973
2.9 µg/L	6 mo	Brook trout, yearling	gross toxic symptoms observed	CH ₃ HgCl	QCW 1976
0.93 µg/L	Part of 3-year study	Brook trout	spawning occurred at all lower conc., but offspring of parental fish exposed to 0.93 µg/L exhibited reduction in growth 90 d after hatching	CH ₃ HgCl	QCW 1976
0.93 µg/L	24 mo	Brook trout	2nd generation fish developed	CH ₃ HgCl	QCW 1976

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
			behavioural symptoms, not spawn- ing, 94% mortality		
0.29 µg/L	full study	Brook trout	no adver- se effects noted	CH ₃ HgCl	QCW 1976
0.0001 N	50 min	Stickleback, 3-spine	opercular movement rate and percentage normal; O ₂ consump- tion reduc- ed up to 50 min, fish reco- vered when placed in fresh wa- ter	HgCl ₂	Jones 1969
<u>Invertebrates</u>					
not stated	96	Worms	high tolerance; LC ₅₀	pH 6 and 8, 20°C; Fraser River, B.C.	Chapman 1982
0.1 (desig- nated as mercury)	TNS	Tadpoles (<i>Bufo valliceps</i>)	killed		WQC 1971
1.000 (Hg(NO ₃) ₂)	96	Worm	LC ₅₀ ^{1,2}	S, M ³	AWQC 1983
0.080 (Hg(NO ₃) ₂)	96	Snail, adult (<i>Amnicola</i> sp.)	LC ₅₀ ^{1,2}	S, M	AWQC 1983
0.370 (HgCl ₂)	96	Snail (<i>Aplexa hypno- rum</i>)	LC ₅₀ ^{1,2}	S, U	AWQC 1983
2.100 (Hg(NO ₃) ₂)	96	Snail, embryo (<i>Amnicola</i> sp.)	LC ₅₀		AWQC 1983
0.740 (HgCl ₂)	96	Crayfish, adult (<i>Orconectes limosus</i>)	LC ₆₀		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.002 (HgCl ₂)	30 d	Crayfish, juvenile (<i>Orconectes limosus</i>)	LC ₅₀ , unfed		AWQC 1983
<0.002 (HgCl ₂)	30 d	Crayfish, juvenile (<i>Orconectes limosus</i>)	LC ₅₀ , fed		AWQC 1983
0.200 (HgCl ₂)	72	Crayfish, male, mixed ages (<i>Procanbarus clarki</i>)	LC ₅₀		AWQC 1983
0.010 (HgNO ₃) ₂)	96	Scud	LC ₅₀ ^{1,2}	S, M	AWQC 1983
0.020 (HgCl ₂)	96	Crayfish, male, mixed ages (<i>Faxonella clypeatus</i>)	LC ₅₀ ^{1,2}	R, M	AWQC 1983
0.050 (HgCl ₂)	96	Crayfish (<i>Orconectes limosus</i>)	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.200 (HgCl ₂)	72	Crayfish, male, mixed ages (<i>Faxonella clypeatus</i>)	LC ₅₀		AWQC 1983
1.000 (HgCl ₂)	24	Crayfish (0.2 g) (<i>Faxonella clypeatus</i>)	LC ₅₀		AWQC 1983
1.000 (HgCl ₂)	672	Crayfish (1.2 g) (<i>Faxonella clypeatus</i>)	LC ₅₀		AWQC 1983
<u>Microorganisms</u>					
0.7834 (HgCl ₂)	96	Rotifer	LC ₅₀ ^{1,2}		AWQC 1983
0.002442 (HgCl ₂)	96	<i>Daphnia magna</i>	LC ₅₀ ^{1,2}	S, U ³	AWQC 1983
0.002217 (HgCl ₂)	96	<i>Daphnia pulex</i>	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.013 (HgCl ₂)	24	<i>Daphnia magna</i>	LC ₅₀		AWQC 1983
0.030 (HgCl ₂)	48	<i>Daphnia magna</i>	EC ₅₀		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.200 (HgCl ₂)		Bacteria (<i>Escherichia coli</i>)	incipient inhibition		AWQC 1983
0.010 (HgCl ₂)	16	Bacteria (<i>Pseudomonas putida</i>)	incipient inhibition		AWQC 1983
0.018 (HgCl ₂)	72	Protozoan (<i>Entosiphon sulcatum</i>)	incipient inhibition		AWQC 1983
0.015 (HgCl ₂)	48	Protozoan (<i>Chilomonas paramecium</i>)	incipient inhibition		AWQC 1983
0.067 (HgCl ₂)	20	Protozoan (<i>Uronema pardeuzi</i>)	incipient inhibition		AWQC 1983
0.150 (HgCl ₂)	28	Protozoan (<i>Microragma heterostoma</i>)	incipient inhibition		AWQC 1983
0.001; 0.05	not stated	Plankton	growth re- duced by 1/2; growth stops		MHSSW 1976
0.03	not stated	<i>Daphnia magna</i>	threshold		Warnick 1969
.01 to 0.03	not stated	Microlife	lethal		Shaw 1967
0.1 (designat- ed as mercury)	TNS	<i>Daphnia magna</i>	killed		WQC 1971
<0.006	64	<i>Daphnia magna</i>	threshold producing immobili- zation		WQC 1971

NOTE: Results are expressed as mercury, not as the chemical (only those entries from AWQC 1983)

1 or EC₅₀

2 Species mean acute value

3 S = static, R = renewal, FT = flow-through, U = unmeasured, M = measured, BA = bioassay

6.2.2.2 Saltwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
<u>Fish Kill Data</u>					
0.008	240	Marine fish	killed		Wilber 1969
0.1 (CH ₃ HgCl)	48	Mullet, juvenile	lethal (diluted sea-water 9 ‰ salinity)		Weis 1978
<u>Fish Toxicity Tests</u>					
0.098 (HgCl ₂)	96	Haddock, larva	LC ₅₀ ^{1,2}	S, U ³	AWQC 1983
0.4530 (HgCl ₂)	96	Mummichog, adult	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.1157 (HgCl ₂)	96	Atlantic silverside, larva, juvenile	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.315 (HgCl ₂)	96	Fourspine stickle- back, adult	LC ₅₀ ^{1,2}	S, U	AWQC 1983
1.678 (HgCl ₂)	96	Winter flounder, larva	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.918 (HgCl ₂)	96	Haddock, embryo	LC ₅₀		AWQC 1983
0.100 (HgCl ₂)	168	Mummichog, adult	LC ₀		AWQC 1983
0.800 (HgCl ₂)	168	Mummichog, adult	LC ₅₀		AWQC 1983
1.000 (HgCl ₂)	168	Mummichog, adult	LC ₁₀₀		AWQC 1983
2.000 (HgCl ₂)	48	Mummichog, adult	LC ₁₀₀		AWQC 1983
0.125 (HgCl ₂)	24	Mummichog, adult	disrupted osmoregu- lation		AWQC 1983
0.012 (HgCl ₂)	28 d	Mummichog, adult	up to 40% reduction in enzyme activity before recovery		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
0.030 to 0.040 (HgCl ₂)	3 d	Mummichog, embryo	many de- velopment- al abnor- malities		AWQC 1983
0.010 to 0.20 (HgCl ₂)	3 d	Mummichog, embryo	some de- velopment- al abnor- malities		AWQC 1983
0.030 to 0.040 (HgCl ₂)	12	Mummichog, embryo	some de- velopment- al abnor- malities		AWQC 1983
0.0674 (HgCl ₂)	32 d	Mummichog, embryo	EC ₅₀		AWQC 1983
0.250 to 5.000 (HgCl ₂)	96	Mummichog, adult	cellular degenera- tion		AWQC 1983
1.150 (HgCL ₂)	96	Mummichog, adult	sluggish, uncoord- inated swimming		AWQC 1983
33.900 (HgCl ₂)	-	Shiner perch	45% re- duction of brain cho- linesterase activity		AWQC 1983
0.005 (HgCl ₂)	30 d	Striped bass, adult	decreased respira- tion 30 d post expo- sure		AWQC 1983
0.010 (HgCl ₂)	60 d	Winter flounder, adult	decreased respira- tion		AWQC 1983
0.125 (CH ₃ HgCl)	24	Mummichog, adult	disrupted osmoregu- lation		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
not stated	not stated	Chinook salmon	Hg concen- trated in liver and kidneys		
not stated	not stated	Pilot whales	heavy metal toxicosis; concentra- ted by 3 to 4 times in tissues of stranded whales		Stoneburner 1978
0.8	96	Fish	LC ₅₀	20°C, 2 ‰ salinity (as HgCl ₂)	Eisler 1977
3.2 x 10 ⁻⁶ mg	1	Japanese eel	accumula- tion in kid- ney; chro- nic dose		WQC 1972
0.6 ng/g	not stated	Cod	concen- trated by 3668 times in gills		WQC 1972
0.30 ng/g	8 d	Pike	concen- trated by 87 times in muscles in 8 days		WQC 1972
3.3	48	Flounder	LC ₅₀ , aerated water		Portman 1970
0.29	48	Marine fish	TL _m		Wilber 1969
<0.003	not stated	Salmon eggs	severe deformity		WQC 1972
0.01 (CH ₃ HgCl)	4, 7, 10, 13 d	Mullet, juvenile	caudal fin rege- neration signifi- cantly retarded all times	diluted sea- water, 9 ‰ salinity	Weis 1978

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
0.001 (CH ₃ HgCl)	4, 7, 10, 13 d	Mullet, juvenile	caudal fin rege- neration became signifi- cant only at later mea- surements	diluted sea- water, 9 ‰	Weis 1978
<u>Invertebrates</u>					
0.09798 (HgCl ₂)	96	Polychaete worm, adult, juvenile	LC ₅₀ ^{1,2}	S, U ³	AWQC 1983
0.070 (HgCl ₂)	96	Sand worm, adult	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.014 (HgCl ₂)	96	Polychaete worm, larva	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.0058 (HgCl ₂)	96	Blue mussel	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.089 (HgCl ₂)	96	Bay scallops, juvenile	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.005944 (HgCl ₂ , HgNO ₃) ₂	96	Pacific oyster	LC ₅₀ ^{1,2}	S, M	AWQC 1983
0.007558 (HgCl ₂)	96	Eastern oyster	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.08412 (HgCl ₂)	96	Brackish water clam, adult	LC ₅₀ ^{1,2}	S, M	AWQC 1983
0.0048 (HgCl ₂)	96	Quahog clam	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.400 (HgCl ₂)	96	Soft-shell clam, adult	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.079 (HgCl ₂)	96	Copepod (<i>Pseudodiap- tomus coronatus</i>)	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.158 (HgCl ₂)	96	Copepod (<i>Emrytemora affinis</i>)	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.010 (HgCl ₂)	96	Copepod (<i>Acartia clausi</i>)	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.01432 (HgCl ₂)	96	Copepod (<i>Acartia tonsa</i>)	LC ₅₀ ^{1,2}	S, U	AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
0.230 (HgCl ₂)	96	Copepod (<i>Nitocra spinipes</i>)	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.0035 (HgCl ₂)	96	Mysid	LC ₅₀ ^{1,2}	FT, M	AWQC 1983
0.017 (HgCl ₂)	96	White shrimp, adult	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.020 (HgCl ₂)	96	American lobster, adult	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.050 (HgCl ₂)	96	Hermit crab, adult	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.0074 (HgCl ₂)	96	Dungeness crab, larva	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.0074 (HgCl ₂)	96	Dungeness crab, larva	LC ₅₀ ^{1,2}	S, M	AWQC 1983
0.014 (HgCl ₂)	96	Green crab, larva	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.060 (HgCl ₂)	96	Starfish, adult	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.150 (CH ₃ HgCl)	96	Amphipod, adult	LC ₅₀ ^{1,2}	S, U	AWQC 1983
0.060 (HgCl ₂)	168	Sand worm, adult	LC ₅₀		AWQC 1983
0.125 (HgCl ₂)	168	Sand worm, adult	LC ₁₀₀		AWQC 1983
0.050 (HgCl ₂)	96	Polychaete worm, adult	LC ₁₃		AWQC 1983
0.0025 to 0.005 (HgCl ₂)	12	Protozoan (<i>Cristigera</i> sp.)	reduced growth		AWQC 1983
1.000 (HgCl ₂)	48	Protozoan (<i>Euplotes vannus</i>)	inhibition of reproduction		AWQC 1983
0.100 (HgCl ₂)	96	Polychaete worm, adult	LC ₆₀		AWQC 1983
0.500 (HgCl ₂)	96	Polychaete worm, adult	LC ₁₀₀		AWQC 1983
0.032 (HgCl ₂)	24	Blue mussel, larva	abnormal development		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
0.032 (HgCl ₂)	24	Pacific oyster, larva	abnormal develop- ment		AWQC 1983
0.012 (HgCl ₂)	12 d	Eastern oyster, embryo	LC ₅₀		AWQC 1983
0.001 (HgCl ₂)	48	Eastern oyster, embryo	LC ₀		AWQC 1983
0.050 (HgCl ₂)	19 d	Eastern oyster, embryo	trace metal upset		AWQC 1983
0.014 (HgCl ₂)	8-10 d	Quahog clam, larva	LC ₅₀		AWQC 1983
0.0025 (HgCl ₂)	42-48	Quahog clam, larva	LC ₀		AWQC 1983
0.001 (HgCl ₂)	168	Soft-shell clam, adult	LC ₀		AWQC 1983
0.004 (HgCl ₂)	168	Soft-shell clam, adult	LC ₅₀		AWQC 1983
0.030 (HgCl ₂)	168	Soft-shell clam, adult	LC ₁₀₀		AWQC 1983
0.050 (HgCl ₂)	1.9	Copepod, adult (<i>Acartia clausi</i>)	LC ₅₀		AWQC 1983
1.000 (HgCl ₂)	48	Barnacle, adult (<i>Balanus balaroidas</i>)	LC ₉₀		AWQC 1983
0.090 (HgCl ₂)	6	Barnacle, cyprid (<i>Balanus balaroidas</i>)	LC ₅₀		AWQC 1983
0.010 (HgCl ₂)	6	Barnacle, cyprid (<i>Balanus balaroidas</i>)	about 10% reduction in sub- strate at- tachment over 19 d		AWQC 1983
0.060 (HgCl ₂)	6	Barnacle, naupilus (<i>Balanus crenatus</i>)	LC ₅₀		AWQC 1983
16.600 (HgCl ₂)	48	Barnacle, cyprid (<i>Balanus improvisus</i>)	about 50% ab- normal develop- ment		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
0.001 (HgCl ₂)	60 d	White shrimp, adult	no effect on respi- ration, growth or molting		AWQC 1983
0.056 (HgCl ₂)	<24	Grass shrimp, larva	LC ₁₀₀		AWQC 1983
<0.0056 (HgCl ₂)	48	Grass shrimp, larva	LC ₀		AWQC 1983
0.010 (HgCl ₂)	48	Grass shrimp, larva	LC ₅₀		AWQC 1983
0.010 to 0.018 (HgCl ₂)	48	Grass shrimp, larva	abnormal develop- ment		AWQC 1983
0.010 (HgCl ₂)	168	Hermit crab, adult	LC ₀		AWQC 1983
0.050 (HgCl ₂)	168	Hermit crab, adult	LC ₅₀		AWQC 1983
0.125 (HgCl ₂)	168	Hermit crab, adult	LC ₁₀₀		AWQC 1983
1.000 (HgCl ₂)	48	Green crab, adult	LC ₅₀		AWQC 1983
1.200 (HgCl ₂)	48	Green crab, adult	LC ₅₀		AWQC 1983
0.010 (HgCl ₂)	47	Green crab, larva	LC ₅₀		AWQC 1983
0.033 (HgCl ₂)	20-30	Green crab, larva	LC ₅₀		AWQC 1983
0.100 (HgCl ₂)	4.3-13.5	Green crab, larva	LC ₅₀		AWQC 1983
1.000 (HgCl ₂)	2.7	Green crab, larva	LC ₅₀		AWQC 1983
3.300 (HgCl ₂)	0.5	Green crab, larva	LC ₅₀		AWQC 1983
10.000 (HgCl ₂)	0.22	Green crab, larva	LC ₅₀		AWQC 1983
0.0018 (HgCl ₂)	8 d	Fiddler crab, zoea	LC ₅₀		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
0.0018 (HgCl ₂)	24	Fiddler crab, zoea	20-100% increase in metabolic rate after stage I zoea		AWQC 1983
0.0018 (HgCl ₂)	5 d	Fiddler crab, zoea	~40% increase in swimming activity of stage V zoea		AWQC 1983
1.000 (HgCl ₂)	28 d	Fiddler crab, adult	low survival, inhibited limb regeneration		AWQC 1983
0.180 (HgCl ₂)	6 d	Fiddler crab, adult	20-25% reduction in percent survival		AWQC 1983
0.180 (HgCl ₂)	24	Fiddler crab, adult	increased O ₂ consumption		AWQC 1983
0.010 (HgCl ₂)	168	Starfish, adult	LC ₀		AWQC 1983
0.020 (HgCl ₂)	168	Starfish, adult	LC ₅₀		AWQC 1983
0.125 (HgCl ₂)	168	Starfish, adult	LC ₁₀₀		AWQC 1983
0.020 (HgCl ₂)	8 min	Sea urchin, spermatozoa	~150% increase in swimming speed		AWQC 1983
2.000 (HgCl ₂)	24 min	Sea urchin, spermatozoa	~80% decrease in swimming speed		AWQC 1983
0.092 (HgCl ₂)	13	Sea urchin, embryo	abnormal development		AWQC 1983

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
0.400 (CH ₃ HgCl)	24	Blue mussel, adult	~90% reduced feeding rate		AWQC 1983
0.050 (CH ₃ HgCl)	19 d	Eastern oyster, adult	trace me- tal upset		AWQC 1983
0.056 (CH ₃ HgCl)	3 d	Amphipod, adult	induced diuresis		AWQC 1983
0.300 to 0.500 (CH ₃ HgCl)	32 d	Fiddler crab, adult	no limb regenera- tion		AWQC 1983
0.100 (CH ₃ HgCl)	32 d	Fiddler crab, adult	melanin absent in regene- rated limbs		AWQC 1983
0.005 (HgCl ₂)	70 d	Copepod, adult (<i>Pseudoca- lanus minutus</i>)	no growth in culture		AWQC 1983
0.001 (HgCl ₂)	70 d	Copepod, adult (<i>Pseudoca- lanus minutus</i>)	no growth inhibition		AWQC 1983
0.078	24	Crustacean	TL ₅₀	Red Sea, 22°C, sali- nity 36 ‰	Hilmy 1981
0.23	96	Mussels	TL ₅₀	Red Sea, 22°C, sali- nity 36 ‰	Hilmy 1981
0.122 (HgCl ₂)	96	Marsh clam, adult	LC ₅₀	salinity 2 ‰	Dillon 1977
0.027	not stated	Bivalve larvae	LC ₅₀		WQC 1972
not stated	96	Worm	lethal	pH 6 and 8, 10 ppt salinity	Chapman 1982
0.075 (HgCl ₂)	48	Prawn	LC ₅₀	aerated	Portman 1970
5.7 (HgCl ₂)	48	Shrimp	LC ₅₀	aerated	Portman 1970

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
9 (HgCl ₂)	48	Cockle	LC ₅₀	aerated	Portman 1970
1.2 (HgCl ₂)	48	Green crab, adult	LC ₅₀	aerated	Portman 1970
4.2 (HgCl ₂)	48	Oyster	LC ₅₀	aerated	Portman 1970
0.005	not stated	Sea urchin, eggs	retards develop- ment		Wilber 1969
0.01	TNS	Sea urchin	severe dis- turbance		OHM-TADS 1981
1.0 (as HgCl ₂)	48	Barnacles, adult	lethal to 90%		WQC 1971
0.1 to 0.33 (HgCl ₂)	96	<i>Crangon crangon</i>	TL _m		WQC 1973
0.08 (HgCl ₂)	48	<i>Dandalus mantanni</i>	TL _m		WQC 1973
0.01 (CH ₃ HgCl)	14 d	Killifish, adult	Some re- tardation of caudal fin regener- ation (seawater, 36 ‰ salinity)		Weis 1978
0.05 (CH ₃ HgCl)	14 d	Killifish, adult	consider- ably more retardation of caudal fish rege- neration than at 0.01 mg/mL (seawater, 36 ‰ salinity)		Weis 1978
2.8 (as HgCl ₂)	1 d	<i>Ambassis safgha</i>	TL _m		WQC 1973
13.1 (HgCl ₂)	2	Mussel, larvae	TL _m	laboratory bioassay	WQC 1973

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
1809 (HgCl ₂)	2	Brine shrimp, larvae	TL _m	laboratory bioassay	WQC 1973
180.9** (HgCl ₂)	2	<i>Crassostrea commercialis</i> , larvae	TL _m	laboratory bioassay	WQC 1973
0.1** (HgCl ₂)	2	<i>Watersipora cucullate</i> , larvae	TL _m	laboratory bioassay	WQC 1973
0.2** (HgCl ₂)	2	<i>Bugula neritina</i> , larvae	TL _m	laboratory bioassay	WQC 1973
0.14** (HgCl ₂)	2	<i>Spirorbis lamellosa</i> , larvae	TL _m	laboratory bioassay	WQC 1973
0.12** (HgCl ₂)	2	<i>Galeolaria caespitosa</i> , larvae	TL _m	laboratory bioassay	WQC 1973
3.3** (HgCl ₂)	48	<i>Platichthys flesus</i>	TL _m	static bio-assay, acute	WQC 1973

1. or EC₅₀
2. Species Mean Acute Value
3. S = static, U = unmeasured, M = measured, FT = flow-through

6.2.2.3 Chronic toxicity of mercury to aquatic life.

Species	Test ¹	Chemical	Limits ² (µg/L)	Chronic Value ² (µg/L)	Reference
<u>Freshwater</u>					
<i>Daphnia magna</i>	LC ³	HgCl ₂	0.72-1.28	0.96	AWQC 1983
<i>Daphnia magna</i>	LC ⁴	HgCl ₂	0.91-1.82	1.287	AWQC 1983
Fathead minnow	LC	HgCl ₂	<0.26 ⁵	<0.26	AWQC 1983
Fathead minnow	ELS	HgCl ₂	<0.23 ⁵	<0.23	AWQC 1983
<i>Daphnia magna</i>	LC ³	CH ₃ HgCl	<0.04 ⁵	<0.04	AWQC 1983
<i>Daphnia magna</i>	LC ⁴	CH ₃ HgCl	0.52-0.87	0.6726	AWQC 1983
Brook trout	LC	CH ₃ HgCl	0.29-0.93	0.5193	AWQC 1983

Species	Test ¹	Chemical	Limits ² (µg/L)	Chronic Value ² (µg/L)	Reference
<u>Saltwater</u>					
Mysid	LC	HgCl ₂	0.8-1.6	1.131	AWQC 1983

1. LC = life cycle or partial life cycle, ELS = early life stage.
2. Results are expressed as mercury, not as the chemical.
3. Flow-through.
4. Renewal.
5. Adverse effects occurred at all concentrations tested.

6.2.2.4 Aquatic Plants.

Conc. (µg/L)	Time (hours)	Species	Result	Reference
<u>Freshwater Species</u>				
1030 (HgCl ₂)	33 d	Alga (<i>Chlorella vulgaris</i>)	EC ₅₀ , cell division inhibition	AWQC 1983
5 (HgCl ₂)	8 d	Blue alga (<i>Microcystis aeruginosa</i>)	incipient inhibition	AWQC 1983
70 (HgCl ₂)	8 d	Green alga (<i>Scenedesmus quadricauda</i>)	incipient inhibition	AWQC 1983
1; 200 (HgCl ₂)	32 d	Water milfoil (<i>Myriophyllum spicatum</i>)	EC ₅₀ , root growth inhibition	AWQC 1983
1598 (CH ₃ HgCl)	168-240	Alga (<i>Ankistrodesmus braunil</i>)	>EC ₅₀ , lipid biosynthesis	AWQC 1983
>2.4 <4.8 (CH ₃ HgCl)	168-240	Alga (<i>Coelastrum microparum</i>)	EC ₅₀ , growth inhibition	AWQC 1983
0.1* mg/L	40	Fungus (<i>Aspergillus niger</i>)	LD ₅₀	Brummond 1971
0.080 (HgCl ₂)	2	Algae, mainly diatoms	EC ₅₀ , reduced photosynthesis	AWQC 1983
2.590 (HgCl ₂)	168-240	Algae (<i>Ankistrodesmus braunil</i>)	EC ₅₀ , inhibited lipid biosynthesis	AWQC 1983
0.030 (HgCl ₂)	96	Green algae (<i>Scenedesmus quadricauda</i>)	incipient inhibition	AWQC 1983

Conc. ($\mu\text{g/L}$)	Time (hours)	Species	Result	Reference
<u>Saltwater Species</u>				
100 (HgCl_2)	10 d	Seaweed (<i>Ascophyllum nodosum</i>)	EC ₅₀ , growth	AWQC 1983
10 (HgCl_2)	5 d	Diatom (<i>Ditylum brightwellii</i>)	EC ₅₀ , growth	AWQC 1983
160 (HgCl_2)	10 d	Seaweed (<i>Fucus serratus</i>)	EC ₅₀ , growth	AWQC 1983
80 (HgCl_2)	10 d	Seaweed (<i>Fucus spiralis</i>)	EC ₅₀ , growth	AWQC 1983
45 (HgCl_2)	10 d	Seaweed (<i>Fucus vesiculosus</i>)	EC ₅₀ , growth	AWQC 1983
50 (HgCl_2)	4 d	Giant kelp (<i>Macrocystis pyrifera</i>)	EC ₅₀ , growth	AWQC 1983
130 (HgCl_2)	10 d	Seaweed (<i>Pelvetia canaliculata</i>)	EC ₅₀ , growth	AWQC 1983
5000 (HgCl_2)	30 min	Red alga (<i>Antithamnion plumula</i>)	LC ₅₀ after 7 d	AWQC 1983
10 (HgCl_2)	4 d	Alga (<i>Chaetoceros galvestonensis</i>)	~30% reduction in growth	AWQC 1983
100 (HgCl_2)	4 d	Alga (<i>Chaetoceros galvestonensis</i>)	no growth of culture	AWQC 1983
100 (HgCl_2)	3 d	Alga (<i>Cyclotella</i> sp.)	no growth of culture	AWQC 1983
2500 (HgCl_2)	-	Alga (<i>Dunaliella</i> sp.)	75% reduction in CO ₂	AWQC 1983
100 (HgCl_2)	8 d	Alga (<i>Dunaliella tertiolecta</i>)	~10% increase in maximum chlorophyll a concentration	AWQC 1983
220 (HgCl_2)	8 d	Alga (<i>Dunaliella tertiolecta</i>)	~45% increase in maximum chlorophyll a concentration	AWQC 1983
10 (HgCl_2)	3 d	Alga (<i>Dunaliella tertiolecta</i>)	~15% reduction in growth	AWQC 1983
2 (HgCl_2)	8 d	Alga (<i>Dunaliella tertiolecta</i>)	no effect on growth	AWQC 1983

Conc. ($\mu\text{g/L}$)	Time (hours)	Species	Result	Reference
5.1 (HgCl_2)	15 d	Alga (<i>Isochrysis galbana</i>)	~10% reduction in growth	AWQC 1983
10.5 (HgCl_2)	15 d	Alga (<i>Isochrysis galbana</i>)	~60% reduction in growth	AWQC 1983
10.5 (HgCl_2)	28 d	Alga (<i>Isochrysis galbana</i>)	growth rate recovery to normal after day 5	AWQC 1983
10 (HgCl_2)	28 d	Kelp (<i>Laminaria hyperborea</i>) zoospores, gametophytes, sporophytes	lowest concentration causing growth inhibition	AWQC 1983
~450 (HgCl_2)	22	Kelp (<i>Laminaria hyperborea</i>) zoospores, gametophytes, sporophytes	EC ₅₀ respiration	AWQC 1983
10 000 (HgCl_2)	28	Kelp (<i>Laminaria hyperborea</i>) zoospores, gametophytes, sporophytes	~80% reduction in respiration	AWQC 1983
50 (HgCl_2)	4 d	Alga (<i>Phaeodactylum tricornutum</i>)	~50% reduction in growth	AWQC 1983
120 (HgCl_2)	4 d	Alga (<i>Phaeodactylum tricornutum</i>)	no growth of culture	AWQC 1983
120 (HgCl_2)	24	Red alga (<i>Plumaria elegans</i>), sporling	40% reduction in growth over 21 d	AWQC 1983
1000 (HgCl_2)	1	Red alga (<i>Plumaria elegans</i>), sporling	40% reduction in growth over 21 d	AWQC 1983
3170 (HgCl_2)	18	Red alga (<i>Plumaria elegans</i>), sporling	LC ₅₀ after 7 d	AWQC 1983
6700 (HgCl_2)	30 min	Red alga (<i>Plumaria elegans</i>), sporling	LC ₅₀ after 7 d	AWQC 1983
8000 (HgCl_2)	30 min	Red alga (<i>Polysiphonia lanusa</i>)	LC ₅₀ after 7 d	AWQC 1983

Conc. (µg/L)	Time (hours)	Species	Result	Reference
10 (HgCl ₂)	10 d	Seaweed, 5 species (<i>Ascophyllum nodosum</i> , <i>Fucus spiralis</i> , <i>F. vesiculosus</i> , <i>F. serratus</i> , <i>Pelvetia canaliculata</i>)	10-30% reduction in growth	AWQC 1983
30 (HgCl ₂)	96	Phytoplankton, natural assemblages	inhibition of growth	AWQC 1983
~170 (CH ₃ HgCl)	10 min	Alga (<i>Dunaliella tertiolecta</i>)	EC ₅₀ photosynthesis	AWQC 1983
~190 (CH ₃ HgCl)	25 d	Alga (<i>Phaeodactylum tricornutum</i>)	EC ₅₀ photosynthesis	AWQC 1983
44 (HgCl ₂)	18	Red alga (<i>Plumaria elegans</i>), sporling	LC ₅₀ after 7 d	AWQC 1983
100 ((CH ₃) ₂ Hg)	3 d	Alga (<i>Chaetoceros</i> sp.)	~75% reduction in growth	AWQC 1983
500 ((CH ₃) ₂ Hg)	3 d	Alga (<i>Cyclotella</i> sp.)	~15% reduction in growth	AWQC 1983
500 ((CH ₃) ₂ Hg)	3 d	Alga (<i>Phaeodactylum</i> sp.)	~45% reduction in growth	AWQC 1983
40 (CH ₃ HgCl)	25 min	Red agla (<i>Plumaria elegans</i>), sporling	EC ₅₀ growth over 21 days	AWQC 1983

* Chemical used or method of concentration expression, e.g., as Hg, not known.

NOTE: Results expressed as mercury, not as the chemical.

6.2.3 Aquatic Studies (WHO 1976; Rabenstein 1978; Weis 1978; Sharpe 1977). With regard to established mercury levels in freshwater fish, an upper limit has been quoted as 150 µg/kg for Canada; this is probably a normal level for fish in uncontaminated water. Fish from contaminated freshwater areas may have values in the 200 to 5000 µg/kg range; in heavily polluted water, the value may be as high as 20 000 µg/kg. The concentration of mercury in marine fish shows considerable variation. Not all the factors are understood, but it is generally realized that the important factors are species of fish, the geographical location, and the age and/or weight of the fish. The highest values of mercury are usually found in those fish at the end of the long food chain.

The mercury levels in most oceanic fish fall in the range 0-500 $\mu\text{g}/\text{kg}$ wet weight. Major exceptions to this rule are the swordfish, tuna, and halibut, which fall in the range 200-1500 $\mu\text{g}/\text{kg}$. Within a given species, the geographic area appears to play a major role, e.g., cod caught near Greenland had values in the 12-36 $\mu\text{g}/\text{kg}$ range, whereas North Sea cod had values in the range 150-195 $\mu\text{g}/\text{kg}$ wet weight. Cod recovered from heavily contaminated water between Denmark and Sweden had values up to 1290 $\mu\text{g}/\text{kg}$.

Metabolic differences may play a role; differences in mercury levels in different species of benthopelagic fish were noted though they had identical feeding habits and ecological requirements and were exposed to mercury in the same area for the same length of time. And as already mentioned, body weight is an important determinant of mercury levels: more body weight, more mercury. This same relationship exists for freshwater fish.

Finally, the sex of the fish may influence the level of mercury. In the spiny dogfish (saltwater), the males had a higher mercury content than did females for a given body weight. It was suggested that this difference may be due to the fact that the males grow more slowly than the females.

The predominant form of mercury in fish is that of methylmercury (CH_3Hg^+). It has been confirmed by measurements in both Sweden and the North American continent that virtually all of the mercury in freshwater fish is in the form of methylmercury compounds. This is also true for marine swordfish and tuna. Exceptions to this rule are Pacific marlin caught off the coast of Hawaii and lake trout. In the former, methylmercury accounts for only a small fraction of the total mercury; in the latter, it accounts for only about 21-35 percent of the total.

In general, methylmercury (CH_3Hg^+) is the primary form of mercury in fish regardless of the nature of the original pollutant. It is felt that the local cycle concept explains the methylmercury in freshwater fish, with dimethylmercury as the key intermediate, while methylmercury in oceanic fish is not well explained. There is no evidence that methylation occurs in the tissue of fish; it is, however, known to occur in the slime on the skin. It is known that methylation significantly increases the ability of mercury to cross biological membranes; it is thought this is why organisms contain mainly methylmercury compounds, especially freshwater species. The methylation process in the marine environment is not well defined. One explanation states that the presence of methylmercury in fish is a food chain biomagnification process resulting from the generalized contamination of the food web by methylmercury. Methylmercury is quite mobile and tends to concentrate in muscle tissue and in the liver and kidney, whereas

inorganic mercury such as mercury (II) chloride is incorporated primarily in the gills. The former is an inhibitor of mitosis and has been shown to be teratogenic in a variety of organisms.

Methylmercury ($\text{CH}_3\text{Hg}^{++}$) is one of the most toxic forms of mercury, causing irreversible damage to the central nervous system. The body burden of methylmercury for most species (and humans) depends mainly on the daily intake and the rate of excretion characteristic of the species. Based on a theoretical equation, it is predicted that the longer the biological half-time, the greater the body burden for a given constant dose, and that the body burden becomes constant after approximately 5 half-times. The half-time for methylmercury in fish is long; thus, it tends to accumulate in the edible tissues of fish throughout their lifetimes.

Even though the above presentation regarding mercury levels in fish and methylmercury ($\text{CH}_3\text{Hg}^{++}$) toxicity is related to chronic toxicity, it is felt to be pertinent to this manual. The final result of a mercury spill into an aquatic systems may be the formation of methylmercury compounds and the generation of a local cycle with its impact on the surrounding aquatic community.

6.3 Toxicity to Other Biota

6.3.1 Mammals. It has been found that seals, a marine mammal situated at the top of the marine food chain, can tolerate high mercury concentrations. Data from harp seal experiments follow (EPS 1979):

Conc. (mg/kg)	Time (days)	Result
0.25 (as CH_3HgCl , oral)	Daily for 60	Blood values were not abnormal
0.25 (as CH_3HgCl , oral)	Daily for 90	Blood values were not abnormal
25.0 (as CH_3HgCl , oral)	Daily for 20	Lethal on day 20; blood level was 26.8 ppm total Hg (19.0 ppm CH_3Hg); liver level was 134 ppm total (127 ppm CH_3Hg); muscle level was 96.7 ppm total (91.5 ppm CH_3Hg)
25.0 (as CH_3HgCl , oral)	Daily for 26	Lethal on day 26; blood level was 30.3 ppm total Hg (23.7 ppm CH_3Hg); liver level was 142 ppm

Conc. (mg/kg)	Time (days)	Result
		total (125 ppm CH ₃ Hg); muscle level was 125 ppm total (115 ppm CH ₃ Hg)

Methylmercury has been shown to be capable of penetrating the placental barrier in seals and is present at birth. Methylmercury tends to be the predominant form of mercury in the muscle of marine mammals; small amounts are often found in the liver and kidneys (EPS 1979). Mercury has been shown to cause central nervous system damage, teratogenesis and tumorigenesis (PTP 1980). Acute poisoning produces gastroenteritis, diarrhea followed by stomatitis, and acute nephritis if the animal survives (Humphreys 1978).

6.3.2 Avian (WQC 1972; WHO 1976; EPS 1979; Stahl 1969).

Conc. ($\mu\text{g}/\text{m}^3$)	Time (hours)	Species	Result	Reference
80	6 h/d, 20 wk	Pigeons	No behavioural, histological or gross signs of mercurialism	Stahl 1969
17 000	14 wk	Pigeons	Notable behavioural changes	Stahl 1969

Animal test data suggest that the effects of inorganic mercury on tissues are generally reversible, with the exception of massive doses of inorganic compounds or prolonged exposure to extremely high concentrations of elemental mercury vapour. Two studies consider that the mode of administration of organic or inorganic mercury in animals is irrelevant. These authors suggest that mercury in animals is much more toxic in the organic form than in the inorganic form, and that it is widely distributed in the body especially in the kidneys and liver and to a lesser extent in the brain. Avians, however, accumulate mercury far more in feathers than in other parts of their bodies. This made it possible to study the mercury content in feathers of Swedish birds collected in the past century. It was determined that the concentration of mercury in the feathers rose dramatically in the years following 1940, which corresponded to the adoption of alkylmercury compounds used as seed dressings. Predatory birds also showed large

increases, while fish-eating birds accumulated lesser but rising levels, indicating increasing mercury contamination of the aquatic environment.

It has been suggested that environmental mercury may impair the reproductive capacity of bird species at the tops of the food chains, e.g., falcons. The hatching ability of herring gull eggs was not deemed affected by contamination ranging from 2 to 16 ppm in the eggs. The mercury found during these tests was mainly in the methylated form. Other tests with birds at contaminated and noncontaminated sites showed a marked decrease in the hatching success of eggs from the contaminated site. Data are conflicting and the results are definitely not conclusive as to the role of mercury in the hatching ability of avian eggs. It is concluded, however, that fish-eating birds are the species most likely to be affected because of their position at the top of the food chain.

Voluminous data concerning the mercury level in various bird species are available. These data readily illuminate the problem, but are not considered essential to this report and are not reported. That mercury is toxic to avian species is established; further contamination resulting from a spill can only add to the ever-increasing problem.

6.3.3 Plants (Stahl 1969). The vapour from metallic mercury has been demonstrated to be harmful to plants. The extent of damage to a particular species of plant depends mainly on factors which influence the vaporization of mercury, e.g., source, temperature, air-flow rate and initial concentration. It is believed the phytotoxicity of mercury compounds is primarily due to the mercury vapours arising from thermal decomposition or catalytic reduction of the compounds to metallic vapour. However, methylmercury compounds have been shown to disturb mitosis in plant cells; short-chain alkylmercury compounds are known to cause chromosome breakage in the cells. Lesions caused by both inorganic and organic compounds of mercury are indistinguishable from those caused by metallic mercury. Generally, injury to plants has been noticed only when the plants have been located in a confined atmosphere containing a source of mercury; however, examples are given where the mercury content of the air was less than $10 \mu\text{g}/\text{m}^3$ and yet severe damage to roses resulted. Damage to certain species of roses usually consists of brown or black discoloration of the leaves, petals, peduncles and corollas of young buds. Further exposure results in greater discoloration, followed by abscission of the leaves and young buds. The injured plants may recover if removed from the contaminating source. Also, plants tend to accumulate large amounts of mercury in leaves and other parts while possibly exhibiting only limited external damage.

Roses appear to be particularly susceptible to poisoning from metallic mercury vapour. Some experimental evidence has demonstrated the injury is caused by metallic mercury vapour arising from the decomposition/reduction of a particular mercury compound. Nine varieties of roses as well as the broad bean, butterfly weed, oxalis and sunflower were found to be particularly susceptible. Plants of intermediate susceptibility were the peach, privet, tomato, geranium and Boston fern. Relatively resistant plants were the aloe, croton, English ivy, oak and pachysandra.

Data have also been accumulated that indicate that certain plants are injured when exposed to mercury fumes resulting from the decomposition of paints containing mercuric fungicides. It has been demonstrated that one fungicide, DPMDS (di-(phenylmercuric) dodeceny succinate), slowly decomposes at room temperature to give metallic mercury vapour. Most experiments carried out or incidences reported have involved roses.

6.3.4 Toxicity to Other Animals and Insects.

Conc. ¹ (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
1.200 (Hg(NO ₃) ₂)	96	Damselfly (unidentified)	LC ₅₀ ²	S, M ³	AWQC 1983
2.000 (HgCl ₂)	96	Mayfly (<i>Ephemera</i> <i>subvaria</i>)	LC ₅₀	S, U	AWQC 1983
2.000 (HgCl ₂)	96	Stonefly (<i>Acronuria</i> <i>lycarias</i>)	LC ₅₀ ²	S, U	AWQC 1983
2.000 (HgCl ₂)	96	Caddisfly (<i>Hydropsyche</i> <i>betteni</i>)	LC ₅₀ ²	S, U	AWQC 1983
1.200 (Hg(NO ₃) ₂)	96	Caddisfly (unidentified)	LC ₅₀ ²	S, M	AWQC 1983
0.020 (Hg(NO ₃) ₂)	96	Midge (<i>Chironomus</i> sp.)	LC ₅₀ ²	S, M	AWQC 1983
0.108, 0.1075 (HgCl ₂)	7-8 d	Marbled salamander (<i>Ambystoma</i> <i>opacum</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.672 (HgCl ₂)	7 d	Pig frog (<i>Rana gryllo</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983

Conc.1 (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.0599 (HgCl ₂)	7 d	River frog (<i>Rana heckscheri</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.0073 (HgCl ₂)	7 d	Leopard frog (<i>Rana pipiens</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.001, 0.0013 (HgCl ₂)	7 d	Narrow-mouthed toad (<i>Gastrophryne carolinensis</i>) embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.040 (HgCl ₂)	7 d	Green toad (<i>Bufo debilis</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.0659 (HgCl ₂)	7 d	Fowler's toad (<i>Bufo fowleri</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.0368 (HgCl ₂)	7 d	Red-spotted toad (<i>Bufo punctatus</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.0104 (HgCl ₂)	7 d	Northern cricket frog (<i>Acris crepitans</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.0024 (HgCl ₂)	7 d	Southern gray tree- frog (<i>Hyla chry- soscelis</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.0028 (HgCl ₂)	7 d	Spring peeper (<i>Hyla crucifer</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.0025 (HgCl ₂)	7 d	Barking tree frog (<i>Hyla gratiosa</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.0024 (HgCl ₂)	7 d	Squirrel tree frog (<i>Hyla squirella</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983
0.0026 (HgCl ₂)	7 d	Gray tree frog (<i>Hyla versicolor</i>), embryo, larva	EC ₅₀ death and deformity		AWQC 1983

Conc. ¹ (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
0.00016 to 0.0002 (HgCl ₂)	11 mo	African clawed frog (<i>Xenopus laevis</i>), embryo, larva	substan- tial mor- tality		AWQC 1983
0.050 to 0.100 (CH ₃ HgCl)	48	Leopard frog (<i>Rana pipiens</i>), tadpole	LC ₁₀₀		AWQC 1983
0.001 to 0.10 (CH ₃ HgCl)	4 mo	Leopard frog (<i>Rana pipiens</i>)	failure to metamor- phose		AWQC 1983
0.012 to 0.016 (CH ₃ HgCl)	5 d	Leopard frog (<i>Rana pipiens</i>), blastula embryo	LC ₅₀		AWQC 1983
0.008 to 0.012 (CH ₃ HgCl)	5 d	Leopard frog (<i>Rana pipiens</i>), gastrula embryo	LC ₅₀		AWQC 1983
0.012 to 0.016 (CH ₃ HgCl)	5 d	Leopard frog (<i>Rana pipiens</i>), neural plate embryo	LC ₅₀		AWQC 1983
0 to 0.004 (CH ₃ HgCl)	96	Leopard frog (<i>Rana pipiens</i>), blastula embryo	EC ₅₀ teratoge- nesis		AWQC 1983
0.008 to 0.012 (CH ₃ HgCl)	96	Leopard frog (<i>Rana pipiens</i>), gastrula embryo	EC ₅₀ teratoge- nesis		AWQC 1983
0.012 (CH ₃ HgCl)	96	Leopard frog (<i>Rana pipiens</i>), neural plate embryo	EC ₅₀ teratoge- nesis		AWQC 1983
0.008 (CH ₃ HgCl)	>2 d	Newt (<i>Triturus viridescens</i>)	delayed limb regene- ration		AWQC 1983
0.300 (CH ₃ HgCl)	17 d	Newt (<i>Triturus viridescens</i>)	death		AWQC 1983
1.000 (CH ₃ HgCl)	8 d	Newt (<i>Triturus viridescens</i>)	death		AWQC 1983
1.100 (CH ₃ HgCl)	93 d	Mink (<i>Mustela vison</i>), adult	histologic evidence of injury		AWQC 1983

Conc. ¹ (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
11.000 (CH ₃ HgCl)	93 d	Mink (<i>Mustela vison</i>), adult	LC ₅₀ in brain tissue		WQC 1983

1. Expressed as mercury, not the chemical shown.
2. Species Mean Acute Value
3. S = static, M = measured, U = unmeasured

6.4 Effect Studies

The effects of mercury per se on organisms are wide-ranging; as can be seen from a review of Section 6, the subject is quite complicated and not easily explained. The organ(s) of predominant concentration certainly depend on the form of the mercury, organic or inorganic, and the nature of the living organism. In general, mercury is both acutely and chronically toxic. It affects the skin and gills of fish, retards development, affects hatchability of fish, affects the liver and kidneys, and in some cases the central nervous system, and accumulates in these organs as well as in muscle. It inhibits mitosis and affects photosynthesis in plants. It may impair reproductive capacity of species at the top of the food chains (for references review entire section).

6.5 Degradation

6.5.1 Biological Degradation (Sax 1979; Coates 1960; WHO 1976; EPS 1979). Two different types of cycle have been suggested for the environmental distribution of mercury. The "global" cycle depends upon the atmospheric circulation of elemental mercury vapour, whereas the "local" cycle is based on an assumed circulation of volatile methylmercury compounds. Most of the mercury in the former is derived from natural sources, and in the latter, from man-made release. Although both are of importance, the latter is of major concern for this manual. All forms of mercury, whether liquid metal, metal vapour, inorganic or organic compound, represent a burden on the environment.

Organo-mercury compounds may be grouped into three categories: the type R-Hg-X (R = organic, X = electronegative species), the type R₂Hg, and mixed types (possibly none of the above and many of which are of unknown constitution). The alkylmercuric compounds (RHgX) are crystalline solids, usually more soluble in organic solvents than in water. When X is highly electronegative (like fluoride, nitrate, sulphate or phosphate), the compounds behave largely as salts, RHg⁺X⁻, and are usually more

soluble in water and alcohol than in nonpolar solvents; if X is chloride, bromide, iodide, hydroxide, etc. or the like, the compounds behave as covalent materials. The chloride melts at 170°C , but tends to decompose even at low temperature to form metallic mercury and dimethylmercury (b.p. 96°C). Dimethyl mercury is highly toxic and undergoes no perceptible decomposition at room temperature. The higher alkyls decompose to give metallic mercury. The dialkyls are mostly monomeric volatile liquids. Dimethylmercury is water insoluble, possesses a very high volatility and is postulated to diffuse from the aquatic environment into the atmosphere. It is subject to removal by rainfall; if the water is acidic, it is subject to conversion to a monomethylmercury compound. Dimethylmercury readily reacts with mercury (II) compounds, e.g., halides, to form two molecules of monomethylmercury halide.

Both forms of mercury, inorganic (e.g., elemental mercury or the sulphide, HgS) and organic, are subject to conversion to other forms in the environment. The inorganic forms undergo environmental transformations mainly by oxidation-reduction reactions; for example, metallic mercury vapour is oxidized to the mercury (II) ion (Hg^{++}) in water in the presence of oxygen. This latter reaction is highly favored when organic substances are present in the aquatic environment. Once formed, the ionic species is capable of forming a wide variety of complexes and chelates with the organic materials. An important reaction would be the one with sulphide ion (S^{-}) to form the highly insoluble mercury (II) sulphide. This latter reaction is likely to occur in anaerobic aquatic environments where the presence of dissolved hydrogen sulphide gas is likely. Further transformation of the stable sulphide in an anaerobic environment does not usually occur. The insoluble sulphide can, however, be oxidized to the soluble sulphite (SO_3^{-}) and sulphate (SO_4^{-}) salts of mercury, which allow the mercury to ionize and take part in subsequent chemical reactions.

In addition to the above mechanism, the mercury (II) ion can be formed by the breakdown of a variety of organic mercury compounds. The alkoxyalkylmercury compounds are very unstable in acid conditions and aryl- and alkylmercury compounds can be degraded in the environment by chemical and physical processes and also by biologically mediated processes.

Mercury (II) ion can undergo two important reactions in the environment, namely reduction to metallic mercury vapour and conversion to methylmercury compounds (CH_3HgX) and dimethylmercury ($(\text{CH}_3)_2\text{Hg}$), and the interconversions between these compounds. The reduction to metallic mercury will occur in nature under

appropriate reducing conditions. The reaction is probably a key process in the "global" cycle of mercury. Also, certain bacteria, particularly of the genus *Pseudomonas*, can convert mercury (II) ion into metallic mercury. The formation of the methylmercury compounds plays a critical role in the "local" cycle of mercury and is of major concern to this manual. It has been demonstrated that biological methylation of mercury can occur in the organic sediments of aquaria and in sediments from fresh and coastal waters.

Methylation of mercury occurs under both anaerobic and aerobic conditions via biochemical routes. Through the anaerobic route is well defined, it is not thought to be a major producer in the aquatic environment (due primarily to the formation of the favored mercury (II) sulphide). The aerobic route involves methylation of mercury that is bound to homocysteine by processes normally responsible for the formation of methionine in the cell. Since, in the aquatic environment under aerobic conditions, the upper sedimentary layers and sedimentary particles suspended in the water may be both aerobic and anaerobic, both routes are possible in oxygenated water. The fastest rates of methylation in the aquatic environment occur in the uppermost part of the organic sediments (aerobic) and on suspended organic matter.

The above is summarized as follows. In the aqueous environment, mercury (II) ion is formed either by oxidation of metallic mercury vapour by physico-chemical processes or by the cleavage of the carbon-mercury bond in organomercury compounds either chemically or enzymatically. The ion then becomes attached to suspended sediments or in the sedimentary layers. After passage of time, it is postulated that large quantities of the inorganic mercury will penetrate through the biologically active upper sedimentary layers to the inorganic mineral layers of sediments where it should remain inactive. Methylation (to both the monomethyl and dimethyl species) of the mercury (II) ions remaining in the surface layers of the sediment will occur. Methylation significantly increases the ability of mercury to cross biological membranes and this is why aquatic organisms contain mainly methylmercury compounds. The origin of methylmercury compounds in marine fish, however, has not been well defined. Methylation is known to occur in the slime covering fish but there is no evidence that methylation occurs in the tissues of fish.

Airborne metallic mercury is liable to both physical and chemical interactions. Physically it may be adsorbed onto airborne particulate materials, but evidence indicates this form accounts for only about 5 percent or less of the total mercury in the atmosphere. The vapour is predicted to distribute more or less evenly between air and water providing it remains in the unoxidized state. It has been shown that in some

specific areas the airborne mercury was composed of mercury (II) ion (Hg^{++}), monomethylmercury ion (CH_3Hg^+), elemental mercury (Hg) and, to a much lesser extent, dimethylmercury (CH_3HgCH_3). It should be pointed out that the latter compound is converted to elemental mercury by ultraviolet light. It was also pointed out in some cases that the source of the methylated species in the air may have been a result of biomethylation in the aqueous environment. It is obvious from the literature that the conversion and interconversion reactions of elemental mercury and its compounds takes place much more readily in the aqueous environment and it is this environment that has received the most study.

It has also been demonstrated that mercuric ion (Hg^{++}) in soil can be converted to methylmercury (CH_3Hg^+). The experiment was carried out with mercury (II) nitrate ($\text{Hg}(\text{NO}_3)_2$). Experiments carried out over soils enriched with mercury (II) chloride (HgCl_2) solutions showed an immediate release of metallic mercury and a subsequent release of methylmercury (CH_3Hg^+) and dimethylmercury ($(\text{CH}_3)_2\text{Hg}$). Accumulation of methylmercury in the soil was not reported, but it could not be concluded whether the loss was due to volatilization or to demethylation. Losses from the soil were influenced by time, temperature, soil moisture, available carbon in the soil and soil texture.

6.5.2 Effects on Sewage/Wastewater Treatment Facilities. A prime function of sewage/wastewater treatment facilities is to lower the chemical/biological oxygen demand (COD/BOD) in the effluent to the environment and a primary means is by bacterial action on the influent. It has been demonstrated that the efficiency of a treatment plant to lower the COD of wastewater was not reduced by mercury (II) ion concentrations of 1.0, 2.1 or 2.5 mg/L. At 5.0 and 10 mg/L, however, the efficiency to lower the COD was significantly retarded (EPA 660/2-77-239).

Conc. (Hg^{++}) (mg/L)	Time (hours)	Removal	Culture
5.0	0.5	60%	sewage organisms-aerobic
5.0	1.0	55%	sewage organisms-aerobic
10	0.5	41%	sewage organisms-aerobic
10	1.0	33%	sewage organisms-aerobic

With respect to BOD, it was shown that mercury (II) ion at a concentration of 0.61 mg/L had an inhibitory effect on sewage organisms.

Conc. (Hg ⁺⁺) (mg/L)	BOD	Seed	Reference
0.61	50% inhibition of O ₂ utilization; chronic dose (TC ₅₀)	Sewage organisms	WQC 1972, 1971
1.0 (as HgCl ₂)	80% inhibition of O ₂ utilization	Organism not stated, laboratory bioassay	WQC 1971
2.0 (as HgCl ₂)	Complete bacteriostasis (absence of BOD)	Sewage organisms	WQC 1971
0.02 to 0.2 (as HgCl ₂)	Slow increase in toxicity to organisms	Sewage organisms	WQC 1971
>0.2 (as HgCl ₂)	Sharp rise in toxicity to organisms	Sewage organisms	WQC 1971

In respirometer tests, toxicity is used in reference to a condition where the oxygen uptake of microorganisms with addition of the test chemical is less than without said chemical. Some researchers define this condition as inhibition, using toxicity only when no oxygen uptake occurs or when substantially depressed. The latter conditions indicates little biological activity is occurring.

6.5.3 Biodegradation/Dissipation Rate. It has been estimated that the Wabigoon River system in Northwestern Ontario will not be cleansed naturally of mercury for at least 100 years (Tataryn 1982). This river system is recognized as a prime example of industrial mercury pollution. Over an 8-year period (1962-1970), a chlor-alkali plant discharged an estimated 9000 kg of mercury into the watercourse. Mercury levels in sediments downstream from the pollution site for a distance of approximately 80 km are above 1 ppm, while those upstream from the site are less than 0.1 ppm. Once the polluted water reaches Clay Lake at the 80 km mark, the sediment apparently has time to settle and in so doing effectively removes some of the adsorbed mercury from further movement. Mercury levels beyond the lake begin to drop into the 0.1 to 1.0 ppm range.

As indicated in Section 6.5.1, metallic mercury in bottom sediments can be converted at varying rates into mercury (II) ions (Hg⁺⁺) and into organomercury species such as the monomethylmercury ion (CH₃Hg⁺) or dimethylmercury ((CH₃)₂Hg) and can thus be more easily transported downstream. Most of the mercury in river water, however, is adsorbed to suspended or settled matter. The part remaining in deep bottom sediment will probably remain inactive and relatively in place. Some may be transported

as metallic mercury with the suspended sediment; converted mercury will certainly be transported in solution or evolved from the aqueous environment. The timing for this scenario to occur is probably measured in years or tens of years. It has been speculated that the major route of "global" transport of mercury is metallic mercury transported in the atmosphere, leaving the aqueous environment in the "localized" realm (Thibodeaux 1979; WHO 1976; EPS 1979).

6.6 Long-term Fate and Effects

6.6.1 Bioaccumulation/Food Chain Concentration Potential. Aquatic plants have been observed to concentrate mercury from water by factors of 10 000 to 60 000, depending on the plant species. Mercury is known to accumulate in sediments where it can be rendered virtually inactive (deep sediment) or converted to methylmercury (CH_3Hg^+). However, contaminated sediment is not deemed a significant direct contributor to plants as most of the mercury is absorbed directly from the water. Mercury dissipation from sediment is slow. One method of dissipation is conversion to organomercury by microorganisms. The rate of this synthesis is dependent on the microorganism populations in the ecosystem. Loss of mercury from plant life is also slow, as little as less than 1 percent per week (EPS 1979).

The accumulation of methylmercury compounds in the aquatic food chain is apparently a more complex process than in the terrestrial case. Once the mercury is methylated in the upper sedimentary layers or in the suspended sediments, it readily dissociates from the particle and is assumed to be rapidly accumulated by living organisms. Methylmercury has never been detected in filtered water, indicating the efficiency of the accumulation process. It accumulates in all species, whether plant or animal, that possess membranes for gas exchange with the aquatic environment. The food chain accumulation in fresh water is proposed as a three-step process. Step one involves accumulation of methylmercury by bottom fauna that are in close proximity to the active sedimentary layers. Step two is the accumulation in species such as the roach, followed by step three which is the accumulation in the large carnivorous fish such as the northern pike. The higher the trophic level of the fish, the more important the intake from food as opposed to uptake of methylmercury directly from water through the gill membranes. It is postulated, however, that for the overall food chain, uptake through the gills is the key process. The accumulation rate was shown to be fast, while the elimination rate was slow, thereby leading to the concentration factors discussed in Table 4. It is expected that the above generalizations of freshwater species would also apply to marine fish (WHO

1976; QCW 1976). Bioconcentration factors of 63 000 for freshwater fish and 10 000 for saltwater fish have been found, confirming the rapid intake, slow output concept. Some specific bioconcentration factors calculated by the U.S. EPA in 1978 are 4525-8376 (rainbow trout), 20 000 (brook trout) and 900-1640 (clams - *Anodonta grandis*, *Lampsitis radiata* and *Lasmigona complanta*) (PTP 1980). In an actual experimental test period of 20 to 48 weeks, several species of fish (one of which was the brook trout - *Salvelinus fontinalis*) accumulated more than 0.5 µg/gm mercury in their tissues from water containing 0.018 to 0.030 µg/L methylmercury. This represents concentration factors from 27 800 to 16 600 (QCW 1976). In water with a mercury content (compounds not specified) of 0.07 ppb, northern pike were found with a concentration factor of 3000. Some actual factors from analyses were 857, 35 714 and 114 286 (WQC 1971). It was also shown that fish associated with aquatic plants containing mercury absorbed up to 10 times more mercury than a control group.

TABLE 4 BIOCONCENTRATION FACTORS (BCF)

Species	Latin Name	Chemical	Time (days)	BCF	Reference
<u>Freshwater Species</u>					
Alga	<i>Synedra ulna</i>	HgCl ₂	0.29	29 000	AWQC 1983
Mussel	<i>Margaritifera margaritifera</i>	Hg(NO ₃) ₂	39	302	AWQC 1983
Scud	<i>Gammarus sp.</i>	HgCl ₂	7	2500	AWQC 1983
Scud	<i>Gammarus sp.</i>	Hg(NO ₃) ₂	7	2500	AWQC 1983
Alga	<i>Scenedesmus obliquus</i>	CH ₃ HgCl	14	2100, max. by 3rd day	AWQC 1983
Alga	<i>Microcystis incerta</i>	CH ₃ HgCl	14	990, max. by 3rd day	AWQC 1983
Mussel	<i>Margaritifera margaritifera</i>	CH ₃ HgCl	57	2463	AWQC 1983
Scud	<i>Gammarus sp.</i>	CH ₃ HgCl	7	~8000	AWQC 1983
Rainbow trout, juvenile	<i>Salmo gairdneri</i>	CH ₃ HgCl	84	4530, whole fish, 5°C	AWQC 1983
Rainbow trout, juvenile	<i>Salmo gairdneri</i>	CH ₃ HgCl	84	6620, whole fish, 10°C	AWQC 1983

TABLE 4 BIOCONCENTRATION FACTORS (BCF) (Cont'd)

Species	Latin Name	Chemical	Time (days)	BCF	Reference
Rainbow trout, juvenile	<i>Salmo gairdneri</i>	CH ₃ HgCl	84	8049, whole fish, 15°C	AWQC 1983
Mosquitofish	<i>Gambusia affinis</i>	CH ₃ HgCl	30	2500, whole fish, 10°C	AWQC 1983
Mosquitofish	<i>Gambusia affinis</i>	CH ₃ HgCl	30	4300, whole fish, 18°C	AWQC 1983
Mosquitofish	<i>Gambusia affinis</i>	CH ₃ HgCl	30	3000, whole fish, 164 mg/kg in food, 10°C	AWQC 1983
Mosquitofish	<i>Gambusia affinis</i>	CH ₃ HgCl	30	27 000, whole fish, 238 mg/kg in food, 26°C	AWQC 1983
Bluegill, juvenile	<i>Lepomis macrochirus</i>	CH ₃ HgCl	28.5	373, whole fish, 9°C	AWQC 1983
Bluegill, juvenile	<i>Lepomis macrochirus</i>	CH ₃ HgCl	28.5	921, whole fish, 21°C	AWQC 1983
Bluegill, juvenile	<i>Lepomis macrochirus</i>	CH ₃ HgCl	28.5	2400, whole fish, 33°C	AWQC 1983
Fathead minnow	<i>Pimephales promelas</i>	HgCl ₂	287	4994, whole body	AWQC 1983
Fathead minnow	<i>Pimephales promelas</i>	CH ₃ HgCl	336	64 000, whole body	AWQC 1983
Brook trout	<i>Salvelinus fontinalis</i>	CH ₃ HgCl	273	19 000, muscle	AWQC 1983
Brook trout	<i>Salvelinus fontinalis</i>	CH ₃ HgCl	273	13 000, whole body	AWQC 1983
Brook trout	<i>Salvelinus fontinalis</i>	CH ₃ HgCl	756	12 000, whole body & muscle	AWQC 1983
Channel catfish, larva, embryo	<i>Ictalurus punctatus</i>	HgCl ₂	10	441-2071	AWQC 1983

TABLE 4 BIOCONCENTRATION FACTORS (BCF) (Cont'd)

Species	Latin Name	Chemical	Time (days)	BCF	Reference
<u>Saltwater Species</u>					
Alga	<i>Chaetoceros galvestonensis</i>	HgCl ₂	4	10 920	AWQC 1983
Alga	<i>Chironomonas salina</i>	HgCl ₂	2	853	AWQC 1983
Alga	<i>Phaeodactylum tricornutum</i>	HgCl ₂	4	7120	AWQC 1983
Alga, mixed	<i>Asterionella japonica</i> plus <i>Diogenes</i> sp.	HgCl ₂	8	3467	AWQC 1983
Brackish water clam	<i>Rangia cuneata</i>	HgCl ₂	14	1130, whole animal	AWQC 1983
Eastern oyster, adult	<i>Crassostrea virginica</i>	HgCl ₂	74	10 000, soft plants	AWQC 1983
Eastern oyster, adult	<i>Crassostrea virginica</i>	CH ₃ HgCl	74	40 000, soft parts	AWQC 1983
American lobster, adult	<i>Homarus americanus</i>	HgCl ₂	30	129, tail muscle	AWQC 1983
Hydilla plants	-	3 mg/L Hg source	45	accumulated 0.83 µg/g net wt of Hg	Panigrahi 1978
Damselfly nymphs	-	0.05 ng/g Hg source	65	655	WQC 1972
Diving Beetles	-	0.05 ng/g Hg source	65	603	WQC 1972
Snails	-	0.05 ng/g Hg source	17	637	WQC 1972
Daddy Longlegs	-	0.05 ng/g Hg source	49	517	WQC 1972

NOTE: Results based on mercury, not chemical

The origin of methylmercury in terrestrial food chains is predominantly the use of mercury fungicides in the treatment of seed grain. The seeds are consumed by

birds or rodents and the latter, in turn, become victims of the large carnivorous birds. Diminished use of methylmercury compounds led to a diminished level in a given terrestrial food chain. Man is at risk mainly through consumption of contaminated animal species, predator fish and other seafoods (WHO 1976).

6.7 Soil (Klusman 1983)

Experiments were carried out with six soils from the Colorado oil shale area exposed to various concentrations of mercury vapour for periods up to 13 months. The temperature at the test site ranged from -25 to 31°C over the time period. The point of the study was not to delineate the acute problems that would be associated with a spill, but to determine the parameters affecting chronic soil adsorption of mercury vapours that may be emitted by the oil shale industry. It is felt, however, that the findings, although possibly specific to the soil types and geographical area, are pertinent to this manual. Improper decontamination of soil or the continued exposure of soil to elemental mercury vapours for a finite time could lead to contamination of soil immediately surrounding the spill site through the adsorption/desorption mechanism.

Moderate quantities of mercury were adsorbed by soils exposed to low levels of mercury vapour for extended periods under field conditions. The amount being adsorbed is influenced by soil characteristics and temperature. It is a dynamic process; desorption occurs if exposure is terminated or if the vapour phase concentration of mercury is reduced. The capacity of the soils to adsorb mercury and the rate of adsorption are strongly influenced by the amount of amorphous oxides, reducible iron and manganese, and surface area of the soil. These properties are influenced by vegetative cover and to a lesser extent by parent material. Adsorption is higher in finer soil. Moisture degrades the adsorption capacity. It was also determined that desorption rates generally reflected those of adsorption, indicating that adsorption is not permanent. Many other references were given that described studies involving other soil types and geographical areas.

7 HUMAN HEALTH

There is a considerable amount of information in the published literature concerning the toxicological effects of test animal and human exposures to mercury. For the purpose of this section, "mercury" includes elemental, inorganic, and organic mercury compounds reflecting the treatment of mercury in the literature. In humans, mercurials have been associated with neurological disorders, sensory impairment, tremors, buccal ulceration, gastrointestinal complaints, and multisystem involvement due to general encephalopathy. Exposures to high levels of mercury have resulted in death in some cases (PTD 1980; Rabenstein 1978; QCW 1976).

No data with regard to carcinogenicity resulting from exposure to inorganic, elemental or organic mercury were found. Nonhuman mammalian species, however, have been shown to suffer tumorigenesis. With respect to mutagenicity, there appears to be a statistical relationship between the frequency of chromosome breakage and blood concentration of methylmercury in Swedish fish eaters. Similar effects are noted for the fruit fly and onion root tip upon exposure to methylmercury and also to phenylmercury. Congenital cerebral palsy was noted in newborn infants after parental exposure to methylmercury from fish. Teratogenicity has been observed in nonhuman mammals upon exposure to mercuric salts (WQC 1971; DPIMR 1981; PTP 1980).

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits

The exposure standards for mercury are based upon prevention of mercurialism. Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
<u>Time-weighted Averages (TWA)</u>			
TLV [®]	USA-ACGIH	0.05 mg/m ³ (all forms except alkyl) as Hg vapour - skin	TLV 1983
PEL	USA-NIOSH	0.05 mg/m ³	NIOSH/OSHA 1981

Guideline (Time)	Origin	Recommended Level	Reference
TLV*	USA-ACGIH	0.01 mg/m ³ (alkyl compounds) - skin	TLV 1983
<u>Short-term Exposure Limits (STEL)</u>			
STEL	USA-ACGIH	0.03 mg/m ³ (alkyl compounds)	TLV 1983
Ceiling	USA-OSHA	0.1 mg/m ³	NIOSH/OSHA 1981
<u>Other Human Toxicities</u>			
IDLH (elemental mercury)	USA-OSHA	28 mg/m ³	NIOSH/OSHA 1981
IDLH (alkyl compounds)	USA-OSHA	10 mg/m ³	NIOSH/OSHA 1981
TC _{LO}		169 µg/m ³	ITII 1981
TC _{LO} (elemental mercury)		150 µg/m ³ (16 d)	RTECS 1979
TD _{LO} (parenterally, elemental mercury)		270 to 40 g	Patty 1981
LD _{LO} (oral, elemental mercury)		1429 mg/kg	Patty 1981
TD _{LO} (oral - woman) (HgCl ₂)		50 mg/kg	RTECS 1979
LD _{LO} (oral) (HgCl ₂)		29 mg/kg	Patty 1981
LD _{LO} (oral) (HgI ₂)		357 mg/kg	Patty 1981
TD _{LO} (oral) (Hg(CN) ₂)		10 mg/kg	Patty 1981

Inhalation Toxicity Index

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

$$ITI = 1315.12 \text{ (Vapour pressure, in mm Hg/TLV}^{\circ}, \text{ in ppm)}$$

$$ITI = 1315.12 \times (0.00120 \text{ mm Hg (20}^{\circ}\text{C)/0.006 ppm)}$$

$$ITI = 2.63 \times 10^2$$

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	May cause dermatitis and/or allergic sensitization following repeated or prolonged skin contact	CSC 1978; NIOSH 1973
Unspecified	Absorption of inorganic mercury through the skin can occur and may contribute to the systemic effects of mercury absorption via other routes	NIOSH 1973
Unspecified	Mercury may be absorbed slowly through the skin. Repeated or prolonged contact may result in poisoning	GE 1977

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
Unspecified	Mercurialentis, deposit of mercury on anterior and posterior surface of lens, may cause constriction of visual fields and blindspots	ITII 1981
Unspecified	When mercury metal droplets are in the epithelium, rather than corneal stroma or anterior chamber, they are extruded rapidly with little reaction	ITII 1981

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: Odourless (NIOSH/OSHA 1981)

Odour Threshold: No data.

7.3.2 Taste. No data.

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
>8.00 mg/m ³ (short-term)	Acute poisoning, gingivitis, stomatitis, nausea, vomiting, diarrhea, kidney damage, respiratory irritation, nerve damage, with an increased chance of death	CSC 1978
8.00 to 1.20 mg/m ³ (short-term)	Acute poisoning, gingivitis, stomatitis, nausea, vomiting, diarrhea, kidney damage, respiratory irritation, nerve damage, death ensues	CSC 1978
1 to 3 mg/m ³ (5 to 2.5 h, estd.) (Hg vapour)	Four workers exposed to mercury while cleaning a storage tank inhaled mercury vapours. Exposure had caused acute mercurial pneumonitis	Milne et al. 1970. <u>IN</u> NIOSH 1973
0.8 to 0.4 mg/m ³ (5 h) (measurement was made 5 days after incident, indicating that levels at time of exposure were much higher, probably near saturation point)	One death and symptoms of chills, nausea, general malaise, tightness in chest and vague respiratory symptoms among eight workers exposed to several tons of mercury following an accidental rupture of tubing in a mercury boiler	Tennant et al. 1961. <u>IN</u> NIOSH 1973
SPECIES: Rabbit		
29 mg/m ³ (30 h)	LC _{LO}	RTECS 1979
29 mg/m ³ (4 h) (Hg vapour)	Severe damage to the kidneys, liver, brain, heart, lungs and colon	Patty 1981
<u>Chronic Exposure</u>		
SPECIES: Human		
8.5 to 1.2 mg/m ³ (Hg vapour)	Acute poisoning characterized by metallic taste, nausea, abdominal pains, vomiting, diarrhea and headache. After a few days the	Patty 1981

Exposure Level (and Duration)	Effects	Reference
>2.0 to 0.1 mg/m ³ (Hg vapour, dust levels undetermined)	saliva glands swell, stomatitis and gingivitis develop. Teeth may loosen and ulcers may form on the lips and cheeks. Mild cases reco- ver within 10 to 14 days 15 of the 30 workers in an open- pit cinnabar mine showed various signs and symptoms suggestive of mercury toxicity consisting of tremor, gingivitis, salivation and irritability	Ladd et al. 1966. <u>IN NIOSH 1973</u>
>2.0 to 0.5 mg/m ³ (form of mercury not specified, but Hg(NO ₃) ₂ was used in the fur felt industry)	Of 1173 hatters, 300 cases of mercury poisoning resulted from exposure. One third of the cases in this exposure range resulted in permanent disability. No cases were reported in workers exposed to levels below 0.1 mg/m ³	Baldi et al. 1953. <u>IN NIOSH 1973</u>
1.00 to 0.30 mg/m ³ (long-term)	Chronic poisoning, loss of weight, loss of appetite, tremors, irrita- bility, gingivitis, stomatitis, salivation, liver and kidney dis- orders, speech imperfections	CSC 1978
1.0 to 0.25 mg/m ³	Two-thirds of 70 female felt hatters showed pronounced symp- toms of mercury poisoning. Hema- tological studies indicated no significant differences in the values of blood elements and hemoglobin levels between these workers and a nonexposed control group	Kesic and Haeusler 1951. <u>IN NIOSH 1973</u>
0.72 to 0.06 mg/m ³ (Hg vapour/aerosol, Hg(NO ₃) ₂ used in industry)	43 of the 529 workers in the hatters' fur-cutting industry had mercury poisoning classified generally as tremor, psychic irrit- ability, vasomotor disturbances and oral conditions	Neal et al 1937. <u>IN NIOSH 1973</u>
0.27 to 0.05 mg/m ³ (long-term)	Insomnia, loss of weight, loss of appetite	CSC 1978
0.27 to 0.01 mg/m ³ (Hg vapour, ~1 yr)	50 workers (9%) complained of loss of appetite, 74 (13%) of loss of weight and 56 (10%) of	Smith et al. 1970. <u>IN NIOSH 1973</u>

Exposure Level (and Duration)	Effects	Reference
	insomnia. In addition to these symptoms, an unstated number of workers with tremors was observed and reported by the examining physicians	
<0.27 to 0.01 mg/m ³ (Hg vapour)	No cases of mercury poisoning diagnosed	Smith et al. 1970. <u>IN NIOSH 1973</u>
>0.1 mg/m ³	In a study of mercury mines and 20 refining plants, noted tremor in only 3 of 22 workers. Sore gums, loose teeth or salivation were observed in 5 of 11 workers	Doc. TLV 1981
0.10 to 0.08 mg/m ³ (Hg vapour)	Study of chlor-alkali workers routinely exposed to mercury vapours. Physical examination showed no evidence of dangerous absorption of mercury among workers	McGill et al. 1964. <u>IN NIOSH 1973</u>
0.1 to 0.05 mg/m ³	75 workers in a scientific glass-ware manufacturing plant exposed to mercury vapours. Only one showed objective tremor, while six reported suffering from insomnia. Upon examination, 59 subjects were found to be myopic	Doc. TLV 1981
SPECIES: Rat (white)		
20-30, 8-10, 2-5 µg/m ³ , (Hg vapour, continuous for 9.5 mo)	Mercury appeared in kidneys, liver and to a lesser extent in the brain and heart. Exhibited pathomorphological changes, disturbances of functional activity of the higher nerve centers	Stahl 1969
SPECIES: Rabbit		
6000 µg/m ³ (Hg vapour, 6 wk)	Severe damage to the kidneys, heart, lungs, and brain	Stahl 1969
SPECIES: Dog		
20 000 µg/m ³ (Hg vapour, few hours)	Death	Stahl 1969

Exposure Level (and Duration)	Effects	Reference
6000 to 20 000 $\mu\text{g}/\text{m}^3$ (Hg vapour, 8 d)	Death	Stahl 1969
3000 to 6000 $\mu\text{g}/\text{m}^3$ (Hg vapour, 40 d)	Affected CNS and digestive tract	Stahl 1969
3000 $\mu\text{g}/\text{m}^3$ (Hg vapour, 40 d)	No signs of intoxication	Stahl 1969
~ 860 $\mu\text{g}/\text{m}^3$ (Hg vapour, 6 wk)	Significant damage to brain and kidney, damage disappeared after subjects were removed from source	Stahl 1969
100 $\mu\text{g}/\text{m}^3$ (Hg vapour, 83 wk)	No damage	Stahl 1969
SPECIES: Dog, Rabbit, Rat		
0.1 to 30 mg/m^3 (Hg vapour, varying times)	Microscopically detectable chan- ges in various organs	WHO 1976
0.9 $\text{mg}/\text{m}^3/12$ wk (Hg vapour)	Kidney and brain damage	WHO 1976
0.1 $\text{mg}/\text{m}^3/>12$ wk (Hg vapour)	No microscopically noticeable damage	WHO 1976

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Human		
Unspecified	A single ingestion of a small amount of pure metallic mercury would not be expected to cause injury. However, if the mercury contained mercury compounds, poisoning could result	GE 1977
>200 g (2-yr-old child)	No adverse reaction	Goldwater 1972

Exposure Level (and Duration)	Effects	Reference
~128 g (female, pregnant)	In a few days, suffered trembling and shaking of the body and loss of muscle power. Symptoms continued for 2 months	Goldwater 1972 (1873 incident)
907 g (woman)	Mercury was fully expelled from for body by the 14th day. Salivation appeared, but rapidly disappeared	Goldwater 1972 (1875 reference)
<u>Chronic Exposures</u>		
SPECIES: Rat		
10 mg/kg/7 d (CH ₃ Hg ⁺)	Kidney damage	WHO 1976
2 mg/kg/unspecified (CH ₃ Hg ⁺ in diet)	Females more sensitive than males, lesions characterized by extrusion of the cytoplasmic masses from proximal tubular cells	WHO 1976
2 mg/kg/9 d (CH ₃ HgCl) (pregnant)	TD _{LO}	RTECS 1979
SPECIES: Mouse		
30 mg/kg/6 d (CH ₃ HgCl) (pregnant)	TD _{LO}	RTECS 1979
SPECIES: Cat		
4067 mg/kg/10-58 d (CH ₃ HgCl) (pregnant)	TD _{LO}	RTECS 1979
SPECIES: Guinea pig		
21 mg/kg	LD ₅₀	RTECS 1979

NOTE: Elemental mercury vapour is known to pass through alveolar and capillary walls where it appears to be readily oxidized to mercury (II) ion. This ion forms soluble compounds with blood, tissue, fluids and proteins, and transport to sensitive organs is effected. The gastrointestinal tract, however, forms a very good barrier and most, if not all, elemental mercury will pass through the digestive system without being absorbed. Increased blood levels of mercury have been observed after ingestion of metallic mercury (Stated to be readily absorbed by the G.I. tract, although occasional incidental swallowing of mercury is without harm (Merck 1983)). As with elemental mercury, inorganic mercury compounds are also only poorly absorbed from the intestine. The latter may be explained by its binding to proteins in the intestinal contents,

rather than to proteins in the first mucosal cells it penetrates. Organomercurials, on the other hand are readily absorbed from the gastrointestinal tract. The elemental mercury that may pass through the barrier will normally concentrate in the kidneys and could ultimately cause damage. Based on review data, it can thus be stated that ingested elemental mercury appears to be much less toxic than inhaled mercury vapour. Mercury compounds, whether organic or inorganic, become widely distributed in all tissues (Stahl 1969; NIOSH 1973; WHO 1976; PC 1984). Obviously, a comprehensive literature search with regard to the effects of ingested elemental mercury was not carried out. Persons interested in more detailed data on the subject are advised to carry out an intensive search of the available literature.

7.4.3 Subcutaneous, Intravenous.

Exposur Level (and Duration)	Effects	Reference
SPECIES: Human		
~270 g (20 mL) (elemental Hg)	Mercury emboli in both lung fields, metal densities in the abdomen and small pools of metal in the right ventricle 2 days after injection. Other symptoms included: slightly elevated temperature, shallow respiration, general malaise, pleuritic chest pains with shortness of breath for 24 hours. Pulmonary function was reduced. Gradual improvement after 5 months without evidence of renal or hepatic damage	Patty 1981
40 to 20 g	Abscess at injection site containing mercury, no other clinical features of mercury poisoning observed	Patty 1981

7.4.4 Carcinogenicity, Teratogenicity, Mutagenicity. No data are available on the teratogenicity or mutagenicity of inorganic mercury in human populations. Furthermore, there is no evidence of mercury exposure producing carcinogenicity (PTP 1980).

Nonhuman mammalian species have been shown to suffer teratogenesis and spontaneous tumorigenesis (PTP 1980). Intraperitoneal injection of metallic mercury in rats has produced sarcomas (NIOSH/OSHA 1981).

7.5 Symptoms of Exposure

Toxicity due to exposure to mercury has been studied for many years and the general symptoms of such exposure are routinely consistent. Such being the case, no specific references are given. In the case of inhalation as the route of entry, the common symptoms have been grouped according to acute and chronic poisoning. Unless specifically stated, the type of mercury is elemental and/or inorganic compounds in the form of vapour, aerosol or dust (Patty 1981; NIOSH 1973; Stahl 1969; PTP 1980; Goldwater 1972).

7.5.1 Inhalation.

7.5.1.1 Acute effects.

1. Metallic taste.
2. Nausea.
3. Abdominal pain.
4. Vomiting.
5. Diarrhea.
6. Albuminuria (sometimes) (albumin in the urine).
7. Respiratory system effects: tightness and pain in chest, dyspnea (difficulty in breathing), coughing, pneumonitis, bronchitis.
8. Erethism (exaggerated emotional response): irritability, temper, excitability, shyness, headache, fatigue, indecision.
9. Salivary glands swell.
10. Stomatitis (inflammation of the mouth).
11. Gingivitis (inflammation of the gums).
12. Teeth may loosen.
13. Ulcers may form on lips and cheeks.
14. Hemolysis (breakdown of the erythrocytes with liberation of hemaglobin).
15. Sleeplessness.
16. Facial tics.
17. Tremor of the digits.
18. Delirium.
19. Hallucinations.
20. Vasomotor disturbances.
21. Pulmonary edema.
22. Death.

7.5.1.2 Chronic effects.

1. Psychic emotional disturbances: irritability, irascibility, inability to concentrate, fearfulness, indecisiveness, depression.
2. Headache.
3. Fatigue.
4. Weakness.
5. Loss of memory.
6. Tumors.
7. Writing affected.
8. Paresthesia.
9. Taste or smell affected.
10. Neuralgia.
11. Dermographism.
12. Renal disease.
13. Chronic nasal catarrh and epistaxis.
14. Salivation.
15. Gingivitis.
16. Digestive disturbances.
17. Ocular lesions.
18. Amblyopia.
19. Narrowing of vision (mainly from organic compounds).

7.5.2 Ingestion. Ingested metallic mercury is not considered toxic until it is absorbed (Dreisbach 1980) (See note in Section 7.4.2 for perspective on this item). The symptoms below are mainly associated with ingestion of inorganic mercury compounds, e.g., mercury (II) chloride.

1. Intense thirst (Lefèvre 1980).
2. Burning in mouth and throat.
3. Stomach or abdominal pains.
4. Nausea and vomiting (vomit may contain blood or greenish substance) (Lefèvre 1980).
5. Diarrhea, occasionally blood-stained or greenish.
6. State of shock (CSC 1978).
7. Kidney damage (NIOSH 1973).

8. Anuria (Dreisbach 1980).
9. Nervous, digestive, urinary, and endocrine systems subject to disturbances (CSC 1978).
10. Irritation and corrosion of tissue.
11. Circulatory collapse.
12. Death.

Note: Once penetration has occurred, symptoms common to inhalation may be apparent.

7.5.3 Skin Contact. The soluble mercury salts are irritating to the skin. They may also penetrate healthy skin. Metallic mercury may cause irritation and is also absorbed through skin. Most cases of dermatitis resulting from exposure to mercury have been principally associated with organic compounds (NIOSH 1973; WHO 1976).

1. Irritation.
2. Inflammation.
3. Blistering (Lefèvre 1980).

7.5.4 Eye Contact. Metallic mercury is not irritating. Insoluble mercury salts are mechanical irritants while soluble salts are chemical irritants to the mucous membranes (Lefèvre 1980). Long-term exposure to mercury vapour produces the appearance of a greyish-brown or yellow haze on the anterior surface of the eye lens (WHO 1976; NIOSH 1973).

1. Irritation.
2. Watering of eyes.
3. Inflammation of conjunctiva.
4. Edema of eyelids (Lefèvre 1980).
5. Occasionally serious lesions in eyes (Lefèvre 1980).
6. Mercurialentis (ITII 1981).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Mercury with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF VIOLENT POLYMERIZATION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION	FORMATION OF TOXIC FUMES	PRESSURIZATION OF VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
<u>GENERAL</u>													
Heat					•								Sax 1979
<u>SPECIFIC CHEMICALS</u>													
Acetylene			•									Forms insoluble, explosive acetyl- ide	NFPA 1978
Ammonia			•										Bretherick 1979
Boron Diiodophos- phide		•										Ignites on con- tact with mercury vapour	Bretherick 1979
Calcium								•					Bretherick 1979
Chlorine		•										Flame forms with Cl ₂ jet over mercury surface at 200-300°C	NFPA 1978
Chlorine Dioxide			•						•				NFPA 1978
Ethylene Oxide			•										Bretherick 1979
Methyl Azide			•									Potentially explosive	Bretherick 1979

8.1 Compatibility of Mercury with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF VIOLENT	DECOMPOSITION POLYMERIZATION	FORMATION OF FLAMMABLE GASES	FORMATION OF TOXIC FUMES	PRESSURIZATION OF VESSELS	SOLUBILIZATION IN CLOSED	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Sodium Carbide (Na ₂ C ₂)												Ground mixtures can react vigorously	NFPA 1978
<u>CHEMICAL GROUPS</u>													
Metals													Bretherick 1979
Oxidizing Agents													Bretherick 1979

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

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

9.1.1 Fire Concerns. Elemental mercury is a noncombustible material (NIOSH/OSHA 1981). Even at room temperature mercury vaporizes to toxic levels; however, when exposed to high temperatures, it readily vaporizes to form extremely toxic fumes. Explosive conditions can occur when mercury is mixed with acetylene, ammonia, chlorine dioxide, nitric acid plus ethanol, and methyl azide (GE 1977).

9.1.2 Fire Extinguishing Agents. Fire extinguishing agents suitable for the combusting materials should be used. Move containers of mercury from the fire area if this can be accomplished without risk. Since elemental mercury readily vaporizes when heated, it is imperative that firefighting personnel wear full protective equipment including self-contained breathing apparatus.

9.1.3 Spill Actions.

9.1.3.1 Spills on land. Spills of elemental mercury on land, whether large (involving single or multiple flashes) or small, should be cleaned up with a suction device. Good quality vacuum cleaners specifically for mercury are available and preferred. Any other type must be equipped with a container suitable to hold mercury and a special filter on the exhaust to prevent emission of vapours. Spilled mercury should be contained by mechanical or chemical barriers to prevent further spreading due to uneven terrain. Recovered mercury should be placed in tightly sealed containers for recycle or disposal. Response personnel should wear protective clothing and a self-contained breathing apparatus.

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

If cleanup is not possible for a length of time, the following are suggested as cover materials to prevent further interactions of mercury with water: inert clays, freshly ground silicates, iron turnings, fluorspar tailings, polymer film overlays, preformed nylon 6, thiols, fibres (containing nylon, cotton and wool), and polyvinyl alcohol gel (containing sulphur or phenyl thiourea) (D'Itri 1977). Sulphur-coated cotton meshwork may also be considered to control erosion, preventing or lessening resuspension of spilled mercury (WPCRS 1972). Overlays with cover materials may prevent movement of the spilled mercury due to turbulence, but will not prevent the methylation process. In general, cover materials may hinder the cleanup effort at some later time, and this should be considered before use.

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills on land. Virtually all of the spilled elemental mercury should have been removed by vacuum cleaner, whether the spill was on a hard surface or on soil. The latter can be easily checked by analytical procedures and if contamination is still present, removal of the surface covering of the soil should complete the process. A spill on a hard surface such as concrete or asphalt would probably be more widespread due to the breaking up of the mercury into small beads upon impact. The cleanup, however, should be easily accomplished by vacuum cleaner. Should analysis of surface scrapings indicate the presence of mercury, calcium polysulphide with excess sulphur can be sprinkled into cracks or other inaccessible places, or onto large areas to convert mercury globules into the sulphide form (GE 1977). This also has the effect of reducing mercury vapour loss during cleanup (NRCC 1979).

9.1.4.2 Spills in water. Every effort should be made to contain the spilled liquid elemental mercury and effect removal by suction techniques as soon after the occurrence as possible. The technique will remove not only free metallic mercury but also mercury adsorbed to sediment as it is expected considerable sediment will be removed in the process. It is mandatory that the effluent from the suction system be placed in an appropriate containment system for further treatment on location or at a waste management facility.

Further treatment of the water body, if required as indicated by water and sediment analysis, can be afforded by methods as explained in Section 9.1.4.3. The carbon adsorption technique, although not applicable in loose form to an environmental aqueous system, is quite effective in removing mercury (II) ion (as HgCl_2). Removal was around 99 percent for carbon dose/initial Hg (II) concentration ratios ranging from 5:1 to 100:1.

Containing the carbon in a "tea bag" reduced this efficiency somewhat (EPA 670/2-75-042).

9.1.4.3 General. A method for the removal of dissolved mercury from water is the precipitation of insoluble mercuric sulphide, which can then be removed by settling or filtration. During the addition of sulphide reagent, the absence of free chlorine is required to prevent the formation of the soluble tetrachloro complex (HgCl_4^-) and sulphate ion (SO_4^-). Care is also required in the quantity of sulphide reagent added to prevent formation of soluble disulphide complexes (NRCC 1979). The process is further detailed below.

Chlor-alkali plant using the mercury-cell process were a major source of mercury contamination prior to the early 1970s. At this time, they began to treat their wastewater with sodium sulphide (Na_2S) or hydrosulphide (NaHS) to convert the mercury in the effluent to mercury (II) sulphide (HgS) which could be precipitated. Further studies of this process showed that a considerable portion of the mercury in the effluent was elemental mercury and that the traditional sulphide treatment was not an effective method for insolubilizing this form of mercury. An oxidizer is required and it was soon shown that an effective oxidizer is a polysulphide (S_n^{2-}), a water-soluble compound of suitable reactivity. It is desirable to maintain a proper sulphide (S^{2-})-polysulphide balance to efficiently oxidize the metallic mercury to mercury (II), with subsequent precipitation as mercury (II) sulphide, while removing the existing mercury (II) ion with existing sulphide ion, a more efficient reaction. Excess sulphide ion must be removed to prevent the formation of the soluble mercury (II) disulphide complex (HgS_2^{2-}). This is accomplished by use of the iron (III) ion (Fe^{+3}), e.g., iron (III) chloride (ferric chloride). It is also important to remove chlorine (Cl_2), hypochlorite (OCl^-) and chlorate (ClO_3^-) ions prior to treatment with the polysulphide agent since these strong oxidants will oxidize sulphide and release the mercury (II) ion. The reducing agent, sodium sulphite (Na_2SO_3), should be added before or concurrent with the addition of the polysulphide agent. It is also important to maintain the pH of the wastewater/contaminated water between 9 and 12. A representative sodium polysulphide treatment solution is prepared by dissolving 2.0 kg of sulphur in 10.0 L of water containing 0.5 kg of sodium sulphide and 0.7 kg of sodium hydroxide and should be freshly prepared. The addition of iron (III) chloride (75-100 ppm) will not only remove excess sulphide, but will also assist in flocculation of the mercury (II) sulphide.

The above treatment for removal of elemental mercury from waste effluent was perfected for treatment of the brine sludge from the chlor-alkali plants, which is usually high in metallic mercury content. The process is also effective in treatment of solid waste to prevent release of elemental mercury in the gas phase and in runoff to waterways. Further treatment with ion-exchange resins and activated carbon is effective in further reducing the residual mercury content (Environ. Sci. Technol. 1981). These processes are explained further below.

Other methods are also available as final steps in routine treatment processes. The Billingsfors Bruks' "BMS process" is primarily intended as a final step in treating wastewater from chlor-alkali plants. It operates at ambient temperature and pressure and will cut the effluent content to at least 10 ppb mercury. The raw effluent is first passed through a sand filter to remove any clays, rust or other solids. The effluent is then treated with sulphuric acid (a 50-60 percent spent sulphuric acid available from plant drying process) to reduce the pH from 10-11 (previous treatment) to 4-5. Chlorine (also from the chlorine plant) is already added to the tank containing the effluent. As the pH is reduced, the chlorine oxidizes any metallic mercury present in the wastewater to the ionic state. At one particular installation, the chlorine present (10-50 ppm) in the sulphuric acid does the job, so a separate chlorine feed is not necessary. Since chlorine poisons the BMS adsorbent (selective for ionic mercury), the wastewater must next be treated with activated carbon to remove any free chlorine that may still be present. The fluid is then treated with the BMS adsorbent which selectively removes the mercury. The adsorbent is prepared from an activated carbon similar in size to the chlorine-removal type. It is made selective to ionic mercury by a concentration of sulphur compounds on its surface. The adsorbent is prepared to contend with wastewater containing about 0.1-0.5 mg/L mercury and has a lifespan of about 1 year. It must, for example, handle wastewater containing 5 mg/L mercury; it will reduce this to about 0.1 mg/L but the lifespan will be reduced. Mercury is recovered from the adsorbent by distillation leaving a safe carbon residue for disposal (Chem. Eng. 1975a).

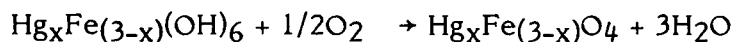
The Imac TMR process is based on ion-exchange and guarantees a mercury effluent of 5 ppb. It is aimed primarily at chlor-alkali plants but may have other applications. The process is operated at ambient conditions. The wastewater to be cleaned first flows into an oxidation reactor together with a slight excess of sodium hypochlorite (NaOCl^- bleach) or chlorine where metallic mercury is oxidized to ionic mercury. The pH is controlled at about 3 to keep any iron in solution. The solution is then filtered through sand or cloth to remove solids and also to retain/oxidize any

mercury droplets that may survive the oxidation step. The liquid is then dechlorinated in a rubber-lined steel column containing a special activated carbon. It then passes to a pair of similarly fabricated vessels containing the ion-exchange resin. The latter is a mercury-selective resin described as a polymeric mercaptan in which thiol groups are attached to a chemically inert and mechanically strong matrix (a macroporous styrene/divinyl-benzene copolymer). The resin contains no nitrogen compounds, to avoid the accidental formation of unstable nitrogen trichloride. The lifespan of the ion exchange resin depends on the input mercury level; for example, with 10 ppm feed mercury, lifespan is 1000 hours and for 1 ppm feed, it is 6 months. Excessive mercury will drastically shorten the lifespan. Normal flow rate is 10 volumes of wastewater per volume resin per hour. Resin can be regenerated up to five times with a hydrochloric acid solution or a special proprietary regenerant. Spent resin contains only about 100 g/m³ of mercury and will not leach out into rainwater or brine. Even though the resin is spent, it is counted as still effective in removing mercury from groundwater (Chem. Eng. 1975a).

The so-called "Re-elixirization" technique is effective at purging mercury and a dozen other metals from effluents such as offgas-scrubbing liquor from municipal waste incineration, wastewater from electroplating of metals, and wastes from chlor-alkali plants. The wastewater is first mixed with an iron (II) salt, usually the sulphate. Typically, two moles or more of salt are needed per mole of metal contaminant. The mixture is neutralized with alkali, forming a dark green hydroxide mixture:



Oxidation with air follows, during which redissolution and complex formation take place, yielding a black ferrite by the reaction:



A magnetic separation removes the insoluble, ferromagnetic ferrite from solution to be used for other purposes or disposal. The process performance shows mercury reductions from 6 mg/L (inlet) to 0.005 mg/L (outlet) and 7.4 mg/L to 0.001 mg/L. The ferrite precipitates do not redissolve and are easy to separate from liquid because of their larger particle size and ferromagnetic behaviour (Chem. Eng. 1975b).

Other methods are described which basically include the typical sulphide precipitation of ionic mercury followed in one case by an oxidation treatment to put both residual metallic mercury and precipitated mercury (II) sulphide into solution as the tetrachloromercury (II) complex (HgCl_4^-). The latter is returned to the chlor-alkali plant

electrolysis cell. Another mercury recovery treatment is primarily concerned with sludge treatment by roasting (Chem. Eng. 1975b).

The following treatment process were studied for treatment of industrial effluents and may have applicability for mercury spill cleanup:

Process	% Removal (TSA 1980)	Process	Highest Observed Removal Efficiency % (EPA 600/8-80-042E)
Biological	51-58	Clarification/Sedimentation	>99
Coagulation/ Precipitation	25-98	Clarification/Sedimentation with Chemical Addition (Alum)	>62
Solvent Extraction	99	Clarification/Sedimentation with Chemical Addition (Alum, Polymer)	88
Carbon Adsorption	80-99	Clarification/Sedimentation with Chemical Addition (Lime)	>96
		Clarification/Sedimentation with Chemical Addition (BaCl ₂)	87
		Clarification/Sedimentation with Chemical Addition (Polymer)	99
		Clarification/Sedimentation with Chemical Addition (Alum, Lime)	71
		Clarification/Sedimentation with Chemical Addition (Ferrous Sulphate, Lime)	>60
		Gas Flotation with Chemical Addition (Calcium Chloride, Polymer)	>90
		Gas Flotation with Chemical Addition (Ferrous Sulphate, Lime, Polymer)	>64
		Granular Media Filtration	86
		Activated Sludge	>87
		Lagoon (Aerated)	>99
		Reverse Osmosis	>60

9.1.5 Disposal. Waste mercury must never be discharged directly into sewers or surface waters. Any recovered contaminated mercury may be purified for reuse or sold to a mercury salvage company when large amounts are involved (GE 1977; NRCC 1979).

9.1.6 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 mercury:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid mercury (NIOSH/OSHA 1981).
- Rubber is recommended for gloves (GE 1977).
- Nonimpervious clothing which becomes contaminated with mercury should be removed promptly and not reworn until the mercury is removed from the clothing (NIOSH/OSHA 1981).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where inorganic mercury is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m ³
Particulate or Vapour Concentration 1 mg/m ³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m ³ or less	Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece.
28 mg/m ³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 28 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m ³
Fire Fighting	operated in pressure-demand or other positive pressure mode. Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against mercury. Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.

9.1.7 Special Precautions. Store mercury in small sealed containers (preferably polyethylene) in a well-ventilated area. Mercury should not be heated without proper precaution to safely handle highly toxic mercury vapours (GE 1977).

9.2 Specialized Countermeasures Equipment, Materials or Systems

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

Recovery from Land

Mercury Vacuum Cleaner

10 PREVIOUS SPILL EXPERIENCE

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

10.1 Truck Spill (PC 1982; HMN 1981).

Several bottles containing mercury broke and spilled their contents as a delivery truck carrying the chemicals entered the loading dock of a university. Mercury was spilled all over the flat bed (wooden) of the truck and some of it seeped through cracks and fell onto the concrete. As the mercury fell onto the concrete, thousands of mercury beads were formed. Approximately 10 kg of mercury were spilled.

Cleanup crews arrived at the site and immediately barricaded the area to prevent public access. The delivery truck was moved to a leveled area to reduce spillage and later moved to a waste management facility for decontamination. The crews wore protective clothing and self-contained breathing apparatus as personal protection. Since the cleanup of mercury from the concrete was requiring more time than expected, the SCBA were depleting rapidly and a central air supply (with appropriate hoses and suits) was used to continuously supply clean air to the cleanup personnel. The beads of mercury on the concrete were picked up using mercury spill kits and a mercury vacuum cleaner. The cleanup took approximately 15 hours to complete. No environmental effects or damage occurred from the spill.

11 ANALYTICAL METHODS

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

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

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

11.1 Quantitative Method for the Detection of Mercury in Air

11.1.1 Flameless Atomic Absorption Spectrophotometry (NIOSH 1977). A range of 0.001 to 1.0 $\mu\text{g}/\text{m}^3$ (0.001-0.12 ppb) of total mercury in particulate, metallic and organic vapour forms in air may be determined by flameless atomic absorption spectrophotometry.

A known volume of air is drawn through a membrane pre-filter ahead of a two-section, solid phase sampling tube containing a 2 mm section of Carbosieve B and a 5 mm section of Silvered Chromosorb P. Generally the flow rate is 1 L/min. Sampling times of 10 min and 1 h are sufficient for ceiling and TWA measurements, respectively.

The membrane filter is digested with 5 mL of concentrated nitric acid in a Teflon decomposition vessel and placed in an oven at 150°C for 1.5 h. The contents of the vessel, after cooling, are quantitatively transferred to a bubbler flask. The volume of liquid in the flask is brought to 75 mL with double-distilled water. One mL of stannous chloride solution (20 percent by weight SnCl_2 in 6 N HCl) is added and air is bubbled through for 4 min at a flow of 1-2 L/min, with a blank sampling tube containing a single section of Silvered Chromosorb P connected to the outlet end of the bubbler system. The Silvered Chromosorb P tube is then purged with pure, dry nitrogen gas for 2 min at

5 L/min and the contents analyzed using the procedure for metallic mercury (as in the procedure for the main solid phase sampling tube). The solid-phase sampling tube is analyzed as two separate sections by thermally desorbing the mercury through the absorption cell of a flameless atomic absorption spectrophotometer. The absorption signals are measured at the 253.7 nm line. For both the membrane filter and the two-section sampling tube, appropriate standard calibration curves and recorder signals are used to quantitate the mercury. This method is preferable since three forms of mercury may be determined in one relatively simple analytical method.

11.2 Qualitative Method for the Detection of Mercury in Air

Mercury in air may be determined by the use of a mercury vapour Drager tube. A volume of air is drawn through a mercury vapour Drager tube using a Drager gas detector pump. A colour change on the indicating layer of the detector tube from pale yellow to orange indicates the presence of mercury vapour. This method may also be used quantitatively depending on the number of pump strokes (Drager 1979).

11.3 Quantitative Method for the Detection of Mercury in Water

11.3.1 Cold Vapour Atomic Absorption (ASTM 1979). A range from 0.2 to 10.0 $\mu\text{g/L}$ (ppb) of total mercury in water may be determined by cold vapour atomic absorption. The method is applicable to fresh and saline waters as well as to industrial or sewage effluents. Both inorganic and organic mercury compounds are determined but must be converted to the mercury (II) ion.

The sample is collected in acid-washed glass or high density polyethylene containers. Immediately after sample collection, the sample is treated with nitric acid to lower the pH to less than or equal to 2.

A 100 mL aliquot of sample is placed in a reaction flask (sample should contain only about 1 μg of mercury). A 5 mL volume of concentrated sulphuric acid and 2.5 mL of concentrated nitric acid are then carefully added with mixing. A 15 mL volume of 5 percent (by weight) potassium permanganate (KMnO_4) solution is then added; an excess may have to be added to maintain a purple colour for at least 15 min. An 8 mL volume of 5 percent (by weight) potassium sulphate solution is then added and the solution heated for 2 h in a water bath at 95°C. The solution is allowed to cool and 6 mL of 12 percent w/v sodium chloride-hydroxylamine sulphate ($\text{NaCl}-(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$) solution is then added. This reduces excess permanganate as is evident by loss of colour in the solution. Stannous sulphate solution is prepared by dissolving 100 g containing 14 mL concentrated sulphuric

acid and diluting to 1 litre. A 5 mL volume of this solution (SnSO_4) is added to the sample solution 30 s after the addition of the sodium chloride-hydroxylamine sulphate solution. The solution is immediately analyzed by cold vapour atomic absorption at 253.7 nm using a standard curve.

11.4 Qualitative Methods for the Detection of Mercury in Water

11.4.1 Mercurous Ion (Welcher 1955). The sample is collected as in Section 11.3, but without the addition of nitric acid. A suitable volume of sample is treated with ammonium hydroxide (1 volume concentrated ammonium hydroxide with 1.5 volumes of water). The formation of a black precipitate indicates the presence of mercury. The precipitate is metallic mercury (black) plus $\text{Hg}(\text{NH}_2)\text{Cl}$ (white).

11.4.2 Mercurous and Mercuric Ions (Welcher 1955). An alternate method may be used. The sample is collected as in Section 11.3, but without the addition of nitric acid. The surface of a piece of copper metal is cleaned with 6 M nitric acid. The nitric acid is then washed off and 4 drops of sample plus 2 drops of 6 M nitric acid are placed on the clean spot. After 5 min, the copper is washed with water and the spot wrapped with a cloth. A bright silvery coating on the copper indicates mercury. This method indicates both mercurous and mercuric ions.

11.5 Quantitative Method for the Detection of Mercury in Soil

11.5.1 Colourimetric (Hesse 1972). A range of 0 to 0.25 μg mercury may be determined in a 40 g sample of soil using the colourimetric method of analysis.

A 40 g sample of soil (seived through a 0.15 mm screen) is placed in a 500 mL, two-necked distilling flask along with 0.1 g of selenium powder. The distillation apparatus consists of a two-necked, round bottom flask containing an air condenser in the vertical position and a gas inlet valve (equipped with an air leak) in the other opening. All gas is introduced through a gas scrubber containing sulphuric acid ($P = 1.84$). The top of the air condenser is connected to a double-surface water condenser, which is connected to another two-necked flask. The latter flask is also connected to two U-tubes containing sufficient water to close the bends. The U-tube train is attached to a water pump. A 50 mL volume of concentrated sulphuric acid and 5 mL of concentrated nitric acid are added. The mixture is digested for 2 h, simmered for an additional 30 min, and allowed to cool. The condenser is slowly rinsed down with 40 mL of water while swirling the flask. The flask is attached to the distillation set-up and 50 mL of concentrated sulphuric acid are added. A slow stream of air must be drawn through the system by means of a water pump

and a partly open air-leak system. The flask is gently heated until two-thirds of the water present has distilled. With the air-free leak system still partly open, a stream of hydrogen chloride gas is passed through the flask at 30 mL/min. The distillation is continued for 2 h and the distillate allowed to cool. The condenser and U-tubes are rinsed with water and the rinsings are added to the distillate. The final volume should be about 125 mL. The distillate is filtered using Whatman 541 paper into a 600 mL graduated beaker and neutralized using concentrated ammonium hydroxide solution. Concentrated hydrochloric acid is added until just acid, then 10 mL of sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$ -pyrosulphite) (20 percent by weight) are added with mixing. A buffer solution is prepared by mixing 50 mL of 1.0 M sodium acetate solution and 13 mL of 1.0 M hydrochloric acid and diluting to 250 mL. A volume of 25 mL of buffer solution and 5 mL of EDTA (ethylenediaminetetraacetic acid) (47 percent by weight of the disodium salt) are added with mixing. The sample is diluted to 250 mL with water, and the pH adjusted to 5. The solution is transferred to a separatory funnel and extracted with 10 mL of dithizone solution. Dithizone stock solution is prepared by dissolving 0.05 g of dithizone in 20 mL of carbon tetrachloride and filtering. The solution is extracted with 100 mL of 5 percent ammonium hydroxide. The alkaline layer is washed twice with 5 mL portions of carbon tetrachloride and is then just acidified with hydrochloric acid and 5 mL of hydroxylamine hydrochloride solution (20 percent w/v) is added. The dithizone solution is extracted with 100 mL of carbon tetrachloride; the organic layer washed twice with 15 mL portions of water and stored in a refrigerator. Just before use, the stock solution is diluted with 10 volumes of carbon tetrachloride. Hydroxylamine hydrochloride solution is prepared by extracting a 20 percent w/v solution with dilute dithizone solution until the extract is colourless after removal of excess dithizone with 5 percent ammonium hydroxide. Any remaining dithizone is extracted with carbon tetrachloride until two successive washings are colourless. The solution is filtered through Whatman 54 paper to remove traces of carbon tetrachloride. The extract from the separatory funnel is placed into a 100 mL separating funnel containing 25 mL of 0.1 M hydrochloric acid. The sample in the original funnel is extracted twice more with 5 mL portions of dithizone; all extracts are added to the 100 mL separatory funnel. The resulting extract is extracted a third time; if the extract changes colour (indicating presence of mercury), it is added to the extract in the 100 mL separatory funnel. A 5 mL volume of the hydroxylamine hydrochloride solution is added to the combined sample extracts in the 100 mL separatory funnel and shaken for 1 min. The organic layer is transferred to a second 100 mL separatory flask containing 50 mL of 0.1 M hydrochloric acid. The aqueous layer from the hydroxylamine

hydrochloride extraction is washed with 5 mL of carbon tetrachloride and the washing is added to the organic layer in the 50 mL of 0.1 M hydrochloric acid. A 2 mL volume of sodium thiosulphate (1.5 percent w/v) is added with shaking. The carbon tetrachloride layer is discarded and the aqueous layer extracted with two 3 mL portions of carbon tetrachloride. To the aqueous layer are added 3 mL of sodium hypochlorite solution containing 5 percent available chlorine. The solution is shaken for 1 min; any evolved chlorine is blown out and the solution shaken. The solution is then extracted with two 3 mL portions of carbon tetrachloride and the extracts discarded.

A 20 mL volume of 1.0 M sodium acetate buffer solution and 5 mL of EDTA solution are added. The solution is mixed and 5 mL of carbon tetrachloride plus 1 mL of dithizone solution are added. After shaking vigorously, the organic layer is added to a clean 100 mL separatory funnel. The aqueous layer is extracted once more with 5 mL of carbon tetrachloride and a few drops of dithizone solution. The organic layer is added to the first. The combined organic layers are extracted with two 15 mL portions of 5 percent ammonium hydroxide solution to remove excess dithizone. The carbon tetrachloride extract is dried with anhydrous sodium sulphate and taken to volume with dried carbon tetrachloride in a 25 mL low actinic glass volumetric flask. The absorbance is determined on a suitable spectrophotometer at 490 nm and the mercury determined using a standard curve.

11.6 Qualitative Method for the Detection of Mercury in Soil

The sample is prepared as in Section 11.5.1. The surface of a piece of copper metal is cleaned with 6 M nitric acid. The nitric acid is then washed off and 4 drops of sample plus 2 drops of 6 M nitric acid are placed on the clean spot. After 5 min, the copper is washed with water and the spot wiped with a cloth. A bright silvery coating on the copper indicates mercury (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	TC _{LO}	toxic concentration low
LD _{LO}	lethal dose low	Td	decomposition temperature
LEL	lower explosive limit	TD _{LO}	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		