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Acute Toxicity of Petrochemical Drilling Fluids Components and Wastes to Fish

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ABSTRACT

During 1972, a study was carried out on the nature and acute toxicity of petrochemical drilling fluids, constituent chemicals and wastes. A field program, conducted in the Mackenzie delta area, N.W.T., was designed to acquire information on the nature and amounts of drilling fluid compounds used, the efficiency of waste containment facilities and on the toxicities of drilling and sumps fluids. A laboratory program determined acute toxicities of drilling fluids and their constituent chemicals through a contract issued to Dr. J. Sprague, University of Guelph. Drilling fluids were acutely toxic with 96 hour LC50's of 0.83 to 12.0 percent using lake chub and rainbow trout. Sump fluids were comparatively less toxic with one sump yielding 96 hour LC50's of 22.5 and 81.0 percent for composite and surface sump fluids, respectively. Out of 27 common components of drilling fluids, seven were toxic and six were moderately toxic. Recommendations on waste containment, treatment and future studies are given. A brief description of the nature and function of drilling fluids and their constituent chemicals is also included.

INTRODUCTION

With the recent increase of petrochemical drilling operations in the Mackenzie River delta area, the possibility of pollution arising from chemicals used in drilling has become important. The current practice of drilling waste disposal in the Northwest Territories is containment within an excavated pit (sump). Upon completion of a drilling operation, the sump is backfilled and incorporated into the permafrost. Since the Mackenzie delta is subject to flooding and erosion, there exists the possibility of contamination of adjacent water bodies by chemicals contained in the sump. Further, with the advent of artificial islands and vessels serving as drilling platforms in the Beaufort Sea, widespread contamination may result.

In order to determine if a pollution problem exists, a study was undertaken from June to August, 1972, by Fisheries Service, in co-operation with the Arctic Petroleum Operators Association (A.P.O.A.). The intent of this study was to assess the nature of drilling fluid components and wastes as well as their acute toxicity to fish.

NATURE AND FUNCTION OF DRILLING FLUIDS

Modern drilling operations employ a rotary system which requires circulation of a drilling fluid or mud (Fig. 1) to remove cuttings from the hole. This fluid is pumped from the surface through the drill pipe and bit, then returned to the surface through the drill pipe annulus. Flow of formation gas, oil and brine into the drill hole is blocked by a fluid column that produces a hydrostatic pressure which counter balances or exceeds formation pressure. Drilled cuttings, after being brought to the surface, are screened from the drilling fluid by shakers located on the drilling platform (Fig. 1) and directed towards a sump. In the Mackenzie delta area sumps are excavated by means of explosives and/or heavy machinery. In addition to cuttings and associated drilling fluid, other substances may be directed towards the sump; these include rig washing compounds, waste lubricants and oils, coolants and domestic waste.

Drilling fluids include liquids, solids and gases suspended in liquids. Most common fluids include suspensions of clays and other solids in water (water base muds), suspension of solids in oil (oil base muds), oil in water clay emulsions (oil emulsion muds), and water in oil emulsions (inverted emulsion muds). Following are descriptions of the more popular mud system classifications in use:

A. Water Base Systems

Low pH:

Fresh water - These have the liquid phase of water containing only small concentrations of salt, and with a pH in the area of 7.0 to 9.5. Included are speed muds, bentonite treated muds, red muds and organic colloid treatments.

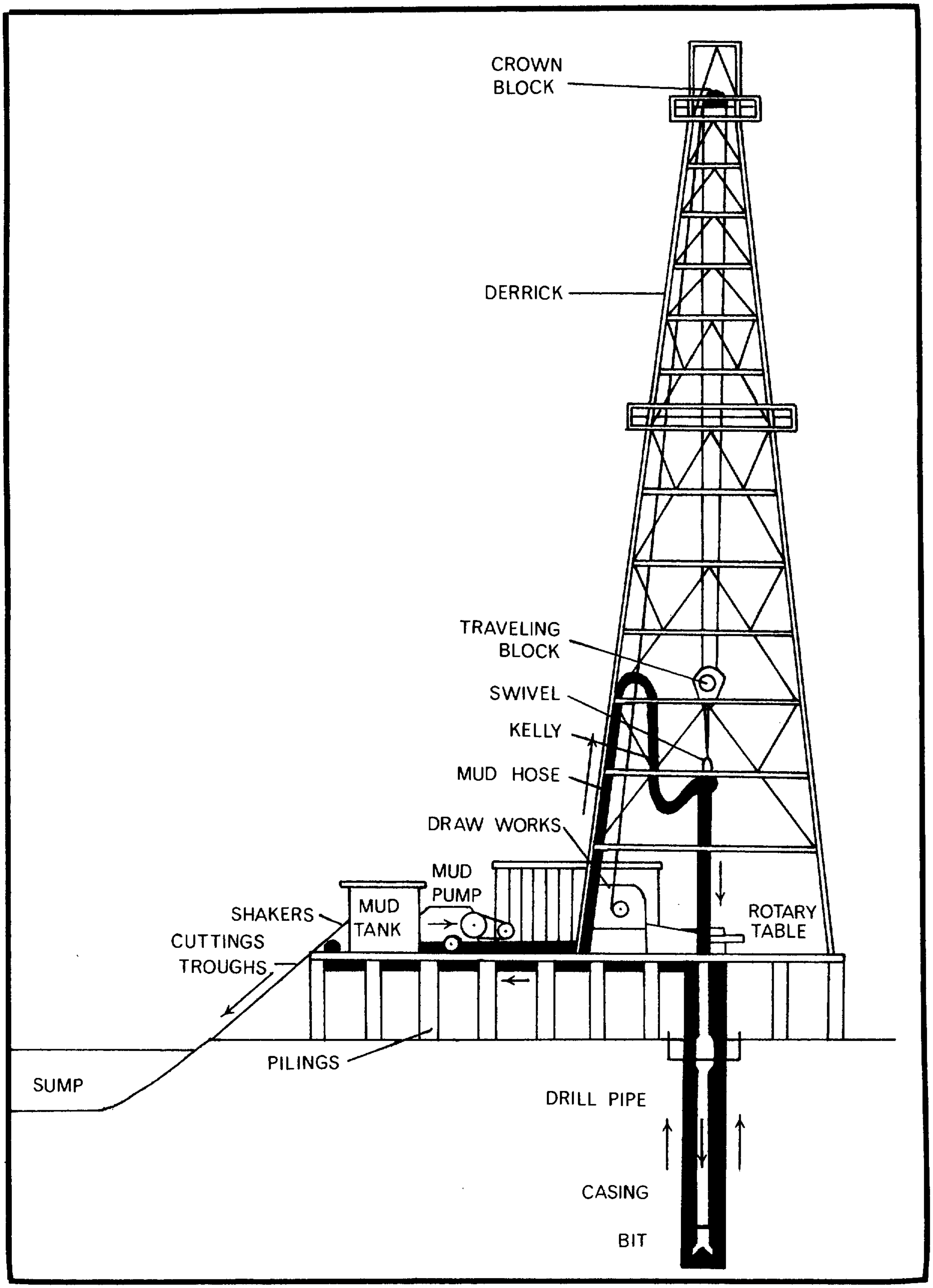

Figure 1. Schematic representation of a drilling rig modified to illustrate the drilling fluid and waste disposal systems.

Brackish water - These include 7.0 to 9.5 pH sea and brackish, or hard water muds. Source water here may be from open seas or bays.

Saturated salt water - The liquid phase of these muds is saturated with sodium chloride, although other salts may be present.

Gyp treated - These gypsum-treated or gyp-based muds are formulated by conditioning the mud with plaster (calcium sulphate).

High pH:

Lime treated - These consist of adding organic caustic soda, lime and clay, and organic thinner and normally have a pH greater than 11.0.

Fresh water - In this system, muds have a liquid phase of fresh water but have been treated with products which bring the pH level above 9.0. These would include most alkaline treated muds.

B. Low Solids Systems

This is a drilling fluid where solids content is less than 10 percent by weight, or a weight less than 9.5 pounds per gallon. A low solid mud may have either a water or oil base.

C. Oil Base Systems

Inverted Emulsion Muds - These water-in-oil muds have water as the dispersed phase and oil as the continuous phase and may contain up to 50 percent by volume of water in the liquid phase.

Oil Base Muds - Usually this is a mixture of diesel fuel and asphalt and is not an emulsion at the start of its use in drilling. Viscosity is controlled by the addition of diesel fuel to thin and asphalt compounds or organic fuel to thicken. Weight is increased by the addition of barites. As a rule, oil muds will either form emulsions with formation water or from other sources of water contamination.

Drilling fluid components are too numerous to describe individually here. Further, the same components may have different brand names according to the company it is produced by. Following are definitions and examples of the major categories of these components which reflect general industry practice and terminology:

Alkalinity and pH Control - These products are designed to control the degree of acidity or alkalinity of a drilling fluid and include lime, caustic soda and bicarbonate of soda.

Bactericides - Function is to reduce bacterial count and include paraformaldehyde, caustic soda, lime and dowcide.

Calcium Removers - Caustic soda, soda ash, bicarbonate of soda and certain polyphosphates make up the majority of chemicals designed to prevent and overcome the contaminating effects of gypsum. Forms of calcium sulphates can reduce the effectiveness of nearly any chemically treated mud not employing calcium removers.

Corrosion Inhibitors - Hydrated lime and amine salts are often added in mud systems to check corrosion. A good mud, containing an adequate percentage of colloids, certain emulsion muds and oil muds exhibits excellent corrosion inhibiting properties.

Defoamers - These are products designed to reduce foaming action, particularly that occurring in brackish water and saturated salt water muds.

Emulsifiers - These function by creating a heterogeneous mixture of two liquids. Included are modified lignosulfonates, certain surface active agents, anionic and nonionic products.

Filter Reducers - Included are bentonite clays, sodium carboxymethyl cellulose and pregelatinized starch. They serve to cut filter loss.

Flocculants - These are used to give increased in gel strength.

Salt, hydrated lime, gypsum and sodium tetraphosphates may be used to cause colloidal particles of a suspension to group, causing solids to settle out.

Foaming Agents - These are most often chemicals which also act as surfactants (surface active agents) to foam in the presence of water. These foams permit air or gas drilling through water making formations.

Lost Circulation Materials - The primary function of lost circulation additives is to plug the zone of fluid loss, back in the formation away from the face of the hole, so that subsequent drilling operations will not disturb the plug.

Lubricants - Extreme pressure lubricants are designed to reduce torque to increase horsepower at the bit by reducing the co-efficient of friction. Certain oils, graphite powder and soaps are used for this purpose.

Shale Control Inhibitors - Gypsum, sodium silicate, calcium lignosulfonates, as well as lime and salt, are products used to control caving by swelling or hydrous disintegration of shales.

Surface Active Agents - Surfactants reduce the interfacial tension between contacting surfaces. These may sometimes be emulsifiers, de-emulsifiers and flocculants.

Thinners, Dispersants - These chemicals modify the relationship between viscosity and percentage of solids in a drilling mud and may further be used to vary the gel strength and increase a mud's pumpability. Tannins, various polyphosphates and lignitic materials are chosen as dispersants, since most of these chemicals also remove solids. Principle purpose of a thinner is to function as a de-flocculant to combat random association of clay particles.

Viscosifiers - Bentonite, sodium carboxymethyl cellulose, attapulgite clays and sub-bentonites are employed as viscosity builders for drilling fluids to assure a high viscosity solids relationship.

Weighting Materials - Barite, lead compounds, iron oxides and similar products possessing high specific gravity are used to control formation pressures, check caving, facilitate pulling dry drill-pipe on the round trip and as an aid in combating circulation loss.

DESCRIPTION OF THE STUDY AREA

Study locations were selected basically by the presence of an active drilling operation at an advanced stage of drilling. Other considerations were proximity to water bodies and cooperation with the company involved. Primary drilling operations studied were: Imperial Oil Ltd. (IOL) Rig 51 on Richards Island (69° 21'N; 134° 52'W) and Gulf Oil Ltd. Rig 15 north of Parsons Lake (69° 51'N; 133° 40'W) (Fig. 2). Samples and supplementary information were also obtained from IOL Rig 49, an active rig north of Rig 51, and IOL Taglu G-33, an abandoned location east of Rig 51.

Richards Island is largely composed of Pleistocene sediments which include stone-free sands, silts and clays. On the north side of the island are Pleistocene remnant hills, ranging in height from 50 to 100 feet. The sediment sequence generally consists of a layer of clay to a depth of 10 feet underlaid by gravel and sand. The north and northeast coasts of Richards Island are receding. This process is enhanced by fall storms with strong N-NW winds. Permafrost underlies most of Richards Island to a depth of approximately 1,200 feet. The active layer fluctuates greatly depending on the proximity of the delta channels. Most of Richards Island is of a very low relief with most of it less than 6 feet above sea level. As a result, flooding in these low-lying areas is an annual event. Peak water levels for the East Channel of the Mackenzie delta (Table 1) illustrate those which may be encountered in the Richards Island area. It should be noted that the 1972 height of 23 feet 5 inches is the greatest in recorded history and caused extensive flooding in the delta area.

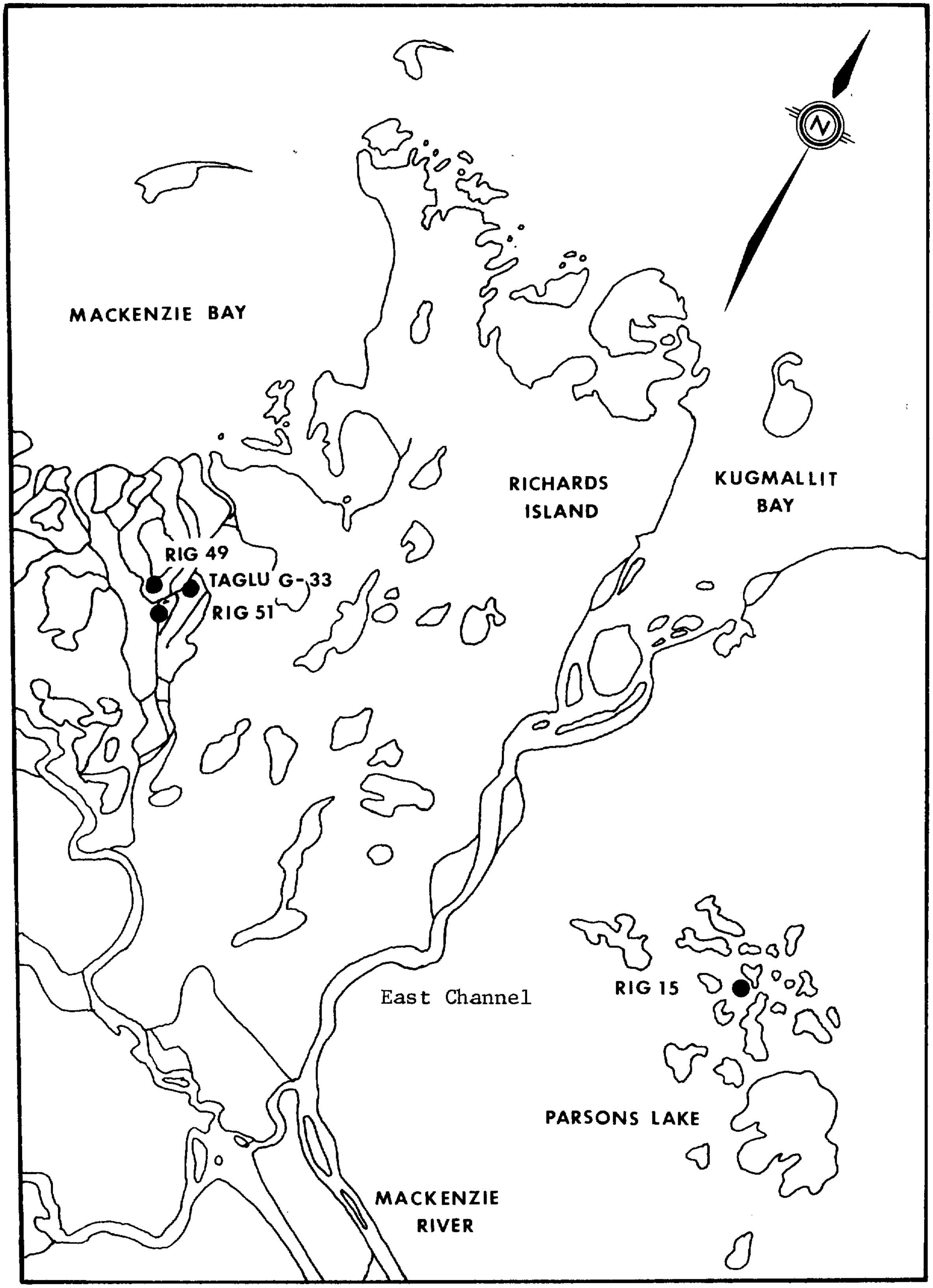

Figure 2. Locations of Mackenzie delta area drilling operations studied during 1972.

Table 1. East Channel ice break-up times and peak water levels at the Inuvik town dock, 1964-72.

Date	Break-up Date		Peak Water Level	
	First Movement	Running Clear	Date	Height*
1964	30/5	7/6	7/6	16' 10"
1965	27/5	9/6	9/6	12' 9"
1966	25/5	9/6	5/6	13' 6"
1967	25/5	5/6	6/6	17' 6"
1968	29/5	8/6	6/6	14' 9"
1969	19/5	4/6	2/6	12' 9"
1970	26/5	3/6	3/6	14' 6"
1971	23/5	2/6	31/5	17' 11"
1972	4/6	12/6	7/6	23' 5"

* In feet and inches above 1965 winter low datum point.

The area north of Parsons Lake is typically tundra with undulating hills and many small irregular thermocarst lakes. Since the elevation at Rig 15 is approximately 200 feet above sea level there was no danger of flooding. Permafrost in this area is usually within one foot of the surface, depending on overburden. Detailed descriptions of the above areas have been given by Mackay (1963). Fish species in these areas may be found in McPhail and Lindsey (1970) and Hatfield et al. (1972).

METHODS AND MATERIALS

Field and laboratory investigations were made into the acute toxicity of petrochemical drilling and waste fluids. The field program was designed primarily to assess the acute toxicity of these fluids utilizing ambient water temperatures, representative diluting water and local fish species. This afforded an opportunity to observe the nature and efficiency of waste containment facilities currently in use. Information on the nature and amounts of drilling fluid components could also be obtained from the drilling supervisors. Another part of the field laboratory program involved chemical analyses carried out on drilling wastes and water samples collected from several Mackenzie delta drilling operations.

The laboratory program was largely designed to assess the acute toxicity of fluid components and other substances used in conjunction with a drilling operation as well as the drilling fluids. This was accomplished through a contract issued to Dr. J. B. Sprague, Department of Zoology, University of Guelph, by Fisheries Service in Winnipeg. The intent of this program was to obtain valid results through experiments carried out under controlled laboratory conditions.

FIELD STUDY:

Bioassays - Static acute toxicity bioassays were carried out at Rigs 51 and 15, using drilling and sump fluids as the test materials. At Rig 51 two single concentration (100%) bioassays were run using surface and composite sump fluid samples. Composite samples were obtained by combining surface and deep aliquots from several locations in the sump. One multiple concentration bioassay was also conducted at Rig 51 using drilling fluid. At Rig 15 three multiple concentration bioassays were carried out using surface sump, composite sump and drilling fluids.

The field bioassay apparatus consisted of six aluminum angle frame cages, each measuring 61 x 30.5 x 30.5 cm, as described by Falk (1973). A 0.64 cm nylon mesh bag was suspended within each cage to support a 4 ml plastic bag. The six cages were lashed together in a 2 x 3 configuration. Test solutions and a control were made up to 20 liters using nearby water bodies as a source of diluting water. These were the Mackenzie River for Rig 51 and a nearby lake for Rig 15. Lake chub *(Couesius plumbius)* were used as the test species for on-site bioassays. They were collected in the Mackenzie River near the town of Arctic Red River using a beach seine and were flown to the test locations in a cooler. Fish were then held in nearby water bodies for a minimum of 48 hours prior to an experiment and allowed to feed on natural food organisms.

Test solutions and the control were aerated prior to and during each experiment. Fish were not introduced to the test solutions until dissolved oxygen levels were above 5 mg/l. Bioassays were run for 96 hours with checks on fish survival, dissolved oxygen and pH, made at 1, 6, 12, 24, 48 and 96 hour intervals. Concentrated test solutions were sufficiently turbid to cause difficulty in obtaining valid dissolved oxygen and pH readings in the field using a Hach Kit. On-site bioassays were run at ambient air temperatures.

In addition to the on-site bioassays, a sample of drilling fluid from Rig 51 was tested in Yellowknife using ninespine sticklebacks *(Pungitius pungitius)*. This experiment was run at the ambient water temperature of a lake near Yellowknife by partly immersing the apparatus along the lake shore. Otherwise, experimental conditions were similar. A portion of the above sample from Rig 51 was forwarded to Winnipeg for supplementary testing, using rainbow trout *(Salmo gairdneri)*. This experiment was run at a constant temperature of 15°C.

For each multiple concentration bioassay outlined above 96 hour LC50's and 95% confidence limits were determined by the method outlined by Litchfield and Wilcoxon (1949). The 96 hour LC50 is the concentration of test material which causes 50% mortality to the test fish after 96 hours.

Caged Fish Experiments - In an effort to determine the survival time of fish in sump fluid under ambient conditions, caged lake chub were immersed in the Rig 51 and Rig 15 sumps near the surface. Cages were galvanized minnow traps (0.64 cm mesh) with the entry holes plugged to prevent the escape of fish. Fish were checked at regular intervals until they were all dead. Ten lake chub were placed in each of two cages.

LABORATORY STUDY:

Bioassays - Prior to commencement of the study, samples of drilling fluid components used in Mackenzie delta operations were obtained from the companies involved. These samples were subsequently forwarded to Dr. J. Sprague. While the field program was underway, "grab" whole drilling fluid samples from Rigs 51 and 15 were also sent to Dr. Sprague for similar testing. Methodology pertaining to these experiments is outlined in the appendix.

Chemical Analyses - Composite sump fluid samples were collected from each location and adjacent water bodies and sent by aircraft for analyses to the Water Quality Division, Environment Canada, Calgary. Analyses performed included a full range of water quality parameters and heavy metal determinations. Analytical methods were those outlined by

Traversy (1971). Bottom samples were collected from Rig 51 sump by an Ekmann dredge and likewise sent to Calgary laboratory for analyses. Analysis was performed for major elements by two methods: (1) leeching with 1N ammonium acetate to determine the level of exchangeable ions, and (2) digestion with Aqua Regia to determine the total level of each ion present, regardless of form.

Composite sump fluid samples were also sent to Mr. D. Shaw, Energy Resources Conservation Board (ERCB), Edmonton, for basic chemical analyses. Toxicity of these samples was also evaluated by placing two rainbow trout (4 - 6 cm) in one liter of clarified fluid after flocculation and filtration. Tests were run at 9°C and the solutions were aerated.

A composite sump fluid sample from Rig 15 was sent to the Environmental Protection Service, (EPS), Winnipeg. Analyses performed on the sample included suspended solids (SS) and chemical oxygen demand (COD).

RESULTS

FIELD STUDY:

From information gathered prior to the study and that gained on-site, a list of drilling fluid components and other substances used during Mackenzie delta area drilling operations was compiled. These, together with a description and functions of the major components, are given in Table 2. Information pertaining to the amount of each constituent chemical used at Rigs 51, 15 and 49 was obtained from the mud logs. At Rig 51 (Table 3) records are not available from late June to late July. However, the components used in the greatest amounts may be noted. These were barium sulphate, bentonite and caustic potash. Large amounts of oilwell and permafrost cement were used during the initial stages of drilling to cement in the surface casings. Also of interest is a change in the amounts of chemicals used with respect to time. This will have a substantial effect in altering the chemical and physical nature of the drilling fluid upon successive sampling. A more complete record of the amounts of the various drilling fluid components used was obtained from Rig 15 (Table 4). Bentonite, oilwell cement, potassium chloride and barium sulphate were the major constituent chemicals. Changes in the amounts of components used with respect to time was also noted. Total amounts of the drilling fluid components used at Rig 49 from May to August are given in Table 5. Major chemicals again were bentonite, barium sulphate and potassium chloride. From Tables 3, 4 and 5 a similarity in the major components used for each drilling operation is evident. This is to be expected since it may be assumed that subterranean features in the general area would be fairly uniform. A change in drilling

Table 2. Nature and function of drilling fluid components used in Mackenzie delta drilling operations.

Name	Description	Function
Gel	Bentonite clay (Wyoming)	Viscosifier, fluid loss reducer
Oilwell cement	-	Seal casing
Permafrost cement	Gypsum, Portland cement, NaCl CFR2	Seal casing
Kelzan XC	Long chain organic polymer	Viscosifier, lubricant
Caustic (Celanese)	NaOH	pH control
Caustic potash	KOH	Fluid loss control, pH control, swelling inhibitor
Potassium chrome alum	$CrK(SO_4) \cdot 12H_2O$	Viscosifier, XC Polymer extender
Peltex or Q-Broxin	Ferrochrome Lignosulfonate	Thinner, dispersant
Plaster of paris	$CaSO_4$ Gypsum	Precipitate soluble calcium Shale control inhibitor
Weight material	$BaSO_4$ Barium Sulphate	Increase mud density
Dowcide	Bactericide	Prevent growth of bacteria
Potassium chloride	KCl	Flocculant
Sodium bicarbonate	$NaHCO_3$	Precipitate soluble calcium pH control
CMC	Sodium carboxymethylcellulose	Fluid loss control

Name	Description	Function
Super-Coll	Treated bentonite	Viscosifier
Uni-Cal	Chrome modified sodium-lignosulfonate	Dispersant, fluid loss control
Ben-Ex	Polyvinyl acetate, maleic anhydride	Increase yield of bentonite
SAPP	Sodium acid pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	Treating cement contamination
Calcium chloride	$CaCl_2$	Flocculant, shale control inhibitor
Skot-Free	Mixed alcohols	Latent liquid solvent
Torq-Trim	Sulfonated triglycerides, aliphatic alcohols, isopropyl alcohol	Surface wetting agent
Tricron	Dihydroxypropane, inorganic salt, tall oil soaps, alkyl aryl sulfonates	Surface wetting agent
B-Free	-	Lubricant
SS-100	Organic polymer	Shale inhibitor, mud stabilizer
Sawdust	-	Fluid loss control
FLR-100	-	Fluid loss reducer
Staflo	-	Filter loss reducer
Metso beads	-	Corrosion control
Paraformaldehyde	CH_2O	Prevent fermentation
Aluminum stearate	$([CH_3(CH_2)_{16}COO]_3Al)$	Defoamer

Table 3. Summary of drilling fluid components and amounts used at IOL Rig 51 from April to August, 1972.

Component	Date	Amount (lb)	Date	Amount (lb)
Bentonite	-	200,000	20/7-17/8	4,400
Oilwell Cement	30/4- 7/5	3,000	-	-
Caustic Soda	30/4-29/6	6,500	20/7-17/8	5,500
Permafrost Cement	30/4- 9/5	198,000	-	-
Kelzan XC	1/5-28/6	3,500	20/7-17/8	300
Potash	1/5- 8/5	58,000	-	-
Chrome Alum	1/5- 8/5	900	-	-
Peltex	19/6-29/6	2,600	20/7-17/8	9,290
Gypsum	10/6	3,050	-	-
Barium Sulphate	20/7-28/6	42,000	20/7-17/8	719,850
Bicarbonate of Soda	-	8,000	-	-

Table 4. Summary of drilling fluid components and amounts used at Gulf Rig 51 from May to August, 1972.

	Date				
Component	1/5-29/5	30/6-22/6	23/6-16/7	17/7-8/8	Total (lb)
Bentonite	92,700	8,700	48,800	84,600	234,800
Caustic Soda	3,050	2,100	3,400	4,450	13,000
CMC	-	150	475	400	1,025
Calcium Chloride	4,800	-	-	-	4,800
Oilwell Cement	328,000	120,000	-	-	448,000
Potassium Chloride	53,100	-	-	-	531,000
Kelzan XC	8,795	-	-	-	8,795
Super-Coll	4,150	37,050	32,450	-	73,650
Bicarbonate of Soda	-	200	-	-	200
Benex Extender	-	8	91	-	99
Ferrochrome Lignosulfonate	-	-	4,350	-	4,350
Unical Thinner	-	-	-	4,855	4,855
Barium Sulphate	-	-	-	371,700	371,700

Table 5. Summary of drilling fluid components and the amounts used at IOL Rig 49 from May to August, 1972.

Component	Amount (lb)
Bentonite	146,200
Caustic Soda	8,000
Peltex	15,525
Barium Sulphate	1,325,200
Kelzan XC	7,875
Chrome Alum	1,090
Dowcide B	30
Potassium chloride	112,800
Bicarbonate of Soda	3,100

fluid composition with respect to time may also be expected since as well depth increases differing subterranean features and pressures will be encountered, requiring change in fluid composition.

Observations on waste containment facilities at each of the active and abandoned drilling operations visited are summarized in Table 6. Sump volumes were calculated using the surface dimensions and average depth. They do not represent the capacity of the sump since maximum sump fluid levels were not encountered. Liners refer to plastic sheets which have been employed in delta operations in an attempt to prevent seepage from the sump. Elevations and distances from adjacent water bodies were estimated from topographical maps. It became evident that the sumps at Rigs 51, 49 and 15 were of adequate size to contain all drilling wastes. However, excavated material which was used as a dyke was generally inadequate to prevent spring floods from washing out the sumps. This was noted at Rigs 51 and 49 which were located about 20 feet above sea-level. Also noted were oil slicks on the surface of the sump as well as strong gasoline or diesel odors.

Table 6. Observations made on drilling waste containment in the Mackenzie delta area.

	Location			
Observation	IOL Rig 51	Gulf Rig 15	IOL Rig 49	IOL Taglu G-33
Sump:				
-length (ft)	200	300	200	200
-width (ft)	190	150	200	100
-depth (ft)	10	8	10	6
-volume (cu ft)	380,000	360,000	400,000	180,000
-odor	Gasoline	Diesel	Diesel	Diesel
-color	Grey-brown	Amber-brown	Grey-brown	Amber-brown
Embankment:				
-height (ft)	0.5-3	1-6	0.5-3	0-2
-material	Silt-clay	Sandy-clay	Silt-clay	Silt-clay
-liner	Present	Absent	Present	Present
Terrain	Flat	Rolling hills	Flat	Flat
Elevation (ft)	20	200	20	20
Adjacent water body	River	Lake	River	River
and distance (ft)	650	1,500	5,000	200

Bioassays - Results from bioassays carried out at Rigs 51 and 15, Yellowknife and Winnipeg, on drilling and sump fluids are summarized in Table 7. Included with these results are the average fish length, liters per gram of fish per day in test solutions, 95% confidence limits for the LC50 and slope (S) of the probit line for each experiment. The 96 hour

LC50's calculated for drilling fluids were 10.3 - 12.0 and 3.55 percent for Rigs 51 and 15, respectively. Those for sump fluids from Rig 15 were 81 percent for a surface sample and 22.5 for a composite sample. Percent survivals from single concentration (100 percent) bioassays carried out at Rig 51 were 90 percent after 74 hours and 80 percent after 96 hours for surface and composite sump fluid samples, respectively.

Caged Fish Experiments - Caged fish placed in Rig 51 sump were all dead after 50 hours, while those placed in the Rig 15 sump were dead after 4 hours. Dissolved oxygen levels ranged from 4 to 5 and 2 to 3 mg/l for Rig 51 and 15 sumps, respectively.

LABORATORY STUDY:

Bioassays - Acute lethal toxicities of drilling fluids and their constituent chemicals are covered in the appendix. These results were submitted in a report by Dr. Sprague. The 96 hour LC50's for drilling fluids were 5.3 and 0.83 percent from Rig 51 and 4.2 percent from Rig 15. Out of 27 drilling fluid components tested 7 were considered to be toxic and 6 were moderately toxic. It should be noted here that the levels of toxicity outlined in the appendix do not conform to those adopted by Environment Canada.

Chemical Analyses - Results from analyses performed on water and sump fluids are summarized in Table 8. Sump fluid samples collected from Rig 51 on June 10 represent conditions in the sump just after flooding, and those collected on June 26 represent those collected 16 days later, when drilling wastes would be more concentrated. Analyses performed on bottom samples were collected just after flooding and 16 days later.

Results from laboratory examination of composite sump fluid samples carried out by the ERCB are summarized in Table 10. Ultra-violet fluorescence was used by this agency as an indication of latent toxicity. It has been found that dark blue-green fluorescence of filtered sump fluid usually signifies that it is non-toxic. However, this proved to be an invalid assessment in the case of the sump fluid sample from Rig 15. The toxic nature of this sump was demonstrated previously (Table 7). It is of interest to note that toxicity occurred only in the sample with a chloride ion concentration of 879 ppm. Mr. Shaw (pers. comm. 1972) has found that sump fluid samples with a chloride concentration greater than 500 ppm are usually lethal to trout.

Table 7. Summary of static acute toxicity bioassays carried out on drilling and sump fluids.

Test Material	Date of: collection of Bioassay	Test Fish	Mean Fork Length (mm)	Temperature °C	Litres/gram of fish/day	96 hour LC50 %	Confidence Limits (P=.95) %	S
Rig 51 1 - Drilling fluid	2-7-72 2-7-72	Lake chub	40.6 (29 - 48)*	8-11	0.62	12.0	7.3 - 19.6	2.17
Rig 51 2 - Drilling fluid	1-9-72 7-9-72	Ninespine sticklebacks	33.8 (30 - 49)	11-13	1.25	10.3	10.2 - 10.4	1.07
Rig 51 3 - Drilling fluid	1-9-72 28-9-72	Rainbow trout	67.2 (51 - 73)	15	0.79	11.2	1.3 - 97.6	1.17
Rig 15 4 - Drilling fluid	30-7-72 30-7-72	Lake chub	52.6 (42 - 62)	10-16	0.31	3.55	2.6 - 4.8	1.84
Rig 15 5 - Composite sump fluid	1-8-72 1-8-72	Lake chub	41.2 (43 - 56)	13-17	0.62	22.5	18.5 - 27.4	1.38
Rig 15 6 - Surface sump fluid	5-8-72 5-8-72	Lake chub	52.2 (37 - 59)	10-17	0.31	81.0	75.6 - 86.6	1.08

* () = Range

Table 8. Summary of water quality parameters determined by the Calgary Water Quality Laboratory for samples collected from sumps and adjacent water bodies during 1972.

Parameter	Rig 51 Sump		Mackenzie River	Rig 51 Sump	Parsons Lake	Rig 49 Sump	Taglu G-33
Sampling date	10/6	26/6	26/6	7/8	7/8	13/7	13/7
Turbidity JTU	-	1000	97	1000	2	-	-
pH	7.9	7.6	8.0	8.2	7.1	8.3	2.4
Cl ppm	-	142.0	4.6	819.0	5.4	-	-
Cu	0.04	0.005	Tr	0.011	0.023	-	-
Fe	-	0.02	-	1.18	0.05	-	-
Pb	0.10	0.038	0.006	0.022	0.006	-	-
Mn	0.22	0.13	Tr	0.372	Tr	-	-
K	64.0	97.15	0.09	320.0	0.6	10.8	3.2
Ca	37.4	42.4	33.2	133.0	10.6	11.1	24.6
SO_4	-	104.0	23.3	510.0	2.9	-	-
Na	42	96.0	4.8	490.0	3.2	114.0	98.0
Zn	0.14	0.02	0.002	0.003	0.012	-	-
As	0.01	0.018	0.004	0.02	0.006	Tr	Tr
N-Kjeldahl	-	6.95	0.67	5.35	0.74	-	-
N-NO_2 & NO_3	-	0.20	0.03	-	0.02	-	-
P-Total	-	1.1	0.18	-	0.018	-	-
P-Ortho	-	0.019	Tr	0.033	0.010	-	-
P-Inorganic	-	0.041	Tr	0.090	-	-	-
C-Inorganic	18.0	40.0	16.0	40.0	4.0	41.0	26.0
C-Organic	32.0	400.0	11.0	385.0	8.0	89.0	40.0
Alkalinity - $CaCO_3$	96.9	158.0	76.6	322.0	29.8	42.9	-
Hardness - $CaCO_3$	-	128.0	102.0	507.0	35.3	35.8	112.0
SiO_2 React.	-	4.7	2.4	6.1	0.2	-	-
Conductance umho/cm	-	1023.0	219.0	4047.0	90.0	-	-

Tr = Trace.

Table 9. Results from analyses carried out on bottom samples collected from the IOL Rig 51 sump

Parameter (ppm dried)	June 10 Leached	June 10 Digested	June 20 Leached	June 20 Digeste
As	0.10	3.3	0.1	3.
Cd	0.13	0.5	-	-
Cu	0.25	191.0	1.3	45.
Pb	4.10	66.0	0.2	6.
Zn	7.90	127.0	15.0	186.
Mn	130.0	280.0	25.0	314.
Co	0.8	11.0	-	-
Ca	1,550.0	2,600.0	2,300.0	4,400.
Mg	244.0	4,100.0	260.0	4,200.
Na	4,100.0	4,170.0	-	-
K	585.0	1,170.0	-	-
Cr	0.3	22.0	-	-
Fe	1.0	23,400.0	2.5	27,600.0
Hg	N.D.	0.3	-	-

N.D. Not detectable.

Supplementary analyses performed on a Rig 15 composite sump field sample by EPS, Winnipeg are given below:

Parameter	mg/l
Chemical oxygen demand	2,622
Total solids	11,583
Suspended solids	7,533
Dissolved solids	4,050

Table 10. Summary of results from laboratory examination of composite sump fluid samples carried out by E.R.C.B.

Determination	Location			
	IOL Rig 51	IOL Rig 49	IOL Taglu G-33	Gulf Rig 15
Appearance	Cloudy amber	Slightly cloudy	Slightly cloudy	Cloudy amber
U. V. Fluorescence	Dark green	Dark green	Green	Dark green
Cl ppm	199	177	32	879
HCO_3	380	328	246	522
CO_3	117	-	29	-
SO_4	186	92	140	496
Ca + Mg	52	101	44	170
Total Solids	1,080	780	580	2,900
pH	8.3	7.3	7.6	7.2
Toxicity	Alive at 96 hours	Alive at 96 hours	Alive at 96 hours	Dead at 67 hours

DISCUSSION

The Canada Fisheries Act specifically prohibits "the deposit of a deleterious substance of any type in water frequented by fish or in any place under any conditions where such deleterious substance or any other deleterious substance that results from the deposit of such deleterious substance may enter any such water". Therefore it has been the policy of the Canada Department of the Environment to limit the deposit of deleterious substances at source and not after dilution in the receiving waters.

Petrochemical drilling wastes, whether drilling or sump fluids, are categorized as industrial effluents. In this regard, the approach taken by the Canada Department of the Environment for effluent regulations involves compliance to a prescribed level of toxicity for each class of industry. This level is being set in view of the best practical waste treatment methods attainable by industry. Current suggested levels include no significant mortality in 65% effluent for the Pulp and Paper Regulations and no less than 50% survival in 100% effluent for the Oil Refinery Regulations over a 96 hour duration.

In addition to these acute toxicity considerations, it is apparent that not enough is known about the sub-lethal, long term and indirect effects of the various classes of effluents. These effects may be manifested through chronic toxicity to aquatic biota, accumulation of toxicants in fish, destruction of food supplies and spawning grounds, and avoidance reactions. All are of great concern to Fisheries Service and are largely unknown without further research.

DRILLING FLUIDS:

In view of the above discussion and results from both the field and laboratory programs, drilling fluids must be considered to be acutely toxic to fish. The current method of waste fluid disposal in an excavated sump for land-based drilling operations virtually precludes discharge of drilling fluids directly into water bodies of the Northwest Territories. Only in the event of flooding of a Rig may these fluids enter water bodies directly. However, with proposed offshore drilling operations in the Beaufort Sea and possibly other areas, containment of wastes fluids may not be possible. In order to comply with pending regulations or guidelines, waste treatment or removal of these wastes may be required.

It was not the intent of this study to determine the mechanism of toxicity or determine specific chemical or physical parameters of the fluids which caused fish mortality. However, there were certain parameters or characteristics which deviated from normal and should be discussed. First are variations in the degree of toxicity with respect to time. A change of the 96 hour LC50 from 0.83 in July to 5.3 percent in September for drilling fluid from Rig 51 may be explained in part by differences in mud composition at a more advanced stage of drilling. Comparisons between field and laboratory bioassays are not practical since experimental conditions and sampling times were different. Suspended solids in drilling fluids were found to be very high but settled rapidly. They may account for some of the direct lethal action of drilling fluids at high concentrations. Such levels of suspended solids released into adjacent water bodies could suffocate benthic fish-food organisms or blanket fish spawning grounds. At lower concentrations poisonous compounds are probably the main active agents. Parameters not determined in the present study such as detergents and bactericides may contribute to this toxicity. High pH values encountered for drilling fluids may further the lethal action of drilling fluids on fish.

DRILLING FLUID COMPONENTS:

From the results and discussion presented in the appendix it became evident that certain constituent chemicals of drilling fluids were "practically non-toxic" while others were "toxic" to fish. Most of the components used in the drilling operation and recorded in the mud logs fell in the "practically non-toxic", "slightly toxic" and "moderately toxic" categories. Further, these components tended to be used in the greatest amounts. A possible means of reducing drilling fluid toxicity, if technically feasible, may be to substitute "non-toxic" chemicals for "toxic" ones, regardless of the amounts used. In addition to the fluid components, other substances used in conjunction with a drilling operation fell in the "toxic" category. They were not recorded in the mud logs and therefore the amounts used are not known. In any event their use should be discontinued and non-toxic substances should be substituted. It is felt that this would assist in reducing the toxicity problem not only of the drilling fluid but also that of sump fluids and prevent adjacent water bodies from being affected through surface runoff.

There is little literature pertaining to the toxicity and effect of drilling fluid components. Daughterty (1951), in experiments using marine invertebrate and fish, found bentonite clay to be non-toxic. Sodium acid pyrophosphate and sodium polyphosphate were lethal to test animals in concentrations ranging from 500 to 7500 ppm. Caustic soda, oilwell cement and white lime were fatal to many test animals from 70 to 450 ppm. Mr. D. Shaw (ECRB, pers.comm) found Peltex to be lethal to trout at 1000 ppm. Kelzan XC Polymer was non-toxic at 500 ppm, while Kelzan Polymer Al was lethal at 5 ppm. There appears to be a lack of specific information on the toxic nature of many chemicals on the market which may be used in drilling fluids. In many cases the toxicity specified by the manufacturer is of questionable validity and does not account for synergistic effects when used in combination with other chemicals.

SUMP FLUIDS:

As expected, sump fluids were comparatively less toxic than drilling fluids. The apparent non-toxic nature of the Rig 51 sump should not be taken as an indication of sump fluids in general. This sump was flooded previously, causing the contents to be flushed into delta channels. In contrast, the Rig 15 sump which was not flooded proved to be acutely toxic. There was a difference in toxicity within the sump with surface fluids being less toxic than deeper fluids. This is believed to be caused by settling of the more toxic agents. Lower toxicity for surface sump fluids at Rig 15 indicates that there is a potential for treatment. By hastening the settling process through flocculating agents, sump fluid toxicity may be further reduced. This is an area that should be further researched. In addition to acute toxicity other chemical and physical characteristics are of concern. As demonstrated in this study, chemical oxygen demand, suspended solids and pH were very high. These parameters should be within acceptable limits as set forth in pending regulations or guidelines before sump fluid release would be permitted. A high chemical oxygen demand is of concern since release of sump fluids into adjacent water bodies may cause oxygen to be depleted. This would result in death of aquatic organisms in this area through suffocation. Other than high chloride levels specific lethal agents of sump fluids cannot be defined. At this time lethality of sump fluids is believed to be due to several factors each acting individually or in combination with each other.

In addition to drilled cuttings and associated drilling fluids, other substances are directed towards the sump. Included among these are rig washing compounds which, as shown in the appendix, were toxic. Substitution of non-toxic compounds for this purpose would assist in reducing sump fluid toxicity. Substances such as waste fuels, lubricants, oils and cooling fluids may be properly incinerated or contained to prevent contamination of adjacent water bodies.

CONCLUSIONS

1. Petrochemical drilling fluids tested during this study were acutely toxic to both local fish in the Mackenzie River delta and Canada's standard bioassay fish, rainbow trout (LC50's<5%).
2. Suspended solids may account for some of the direct lethal action of drilling fluids at high concentrations. However, poisonous components such as chloride are probably the main active agents at lower concentrations.
3. Using the classification adopted by Logan et al. (Appendix), out of 27 common components of drilling fluids tested, 7 were "toxic", 6 were "moderately toxic", 5 were "slightly toxic" and 6 were "practically non-toxic".
4. Toxic substances tested were those comprising minor fractions of the total drilling fluid or those not used in the fluid but for other purposes.
5. Sump fluids are comparatively less toxic than drilling fluids (LC50's 22-80%).
6. Much of the sump fluid toxicity is concentrated in deeper regions of the sump through settling of toxic agents. This may provide a future means of treating sump fluids.

RECOMMENDATIONS

1. From observations made in the field it was noted that sumps were generally provided with inadequate dyking. To insure that sump fluids do not enter water bodies, dykes should be erected to contain all drilling wastes, prevent seepage and preclude flooding.
2. Based on this study's findings, sump and drilling fluids should not be released into water bodies without meeting a prescribed toxicity limit. This level should be set in regulations or guidelines to govern drilling waste disposal and should include limits on hydrocarbons, chemical and biological oxygen demand, suspended solids and pH.
3. Waste fuels, lubricants, detergents and other substances used during a drilling operation which are toxic to fish should be contained and disposed of by means other than discharge into a sump.
4. Since many of the drilling fluid components and other substances tested were acutely toxic to fish an effort should be made to substitute non-toxic chemicals if technically feasible.
5. Future studies should be carried out to define the magnitude of the problem of drilling waste disposal in Canada's north and determine the long term effects on fish and benthic fish-food organisms. Studies should also be directed towards effective and practical waste treatment.

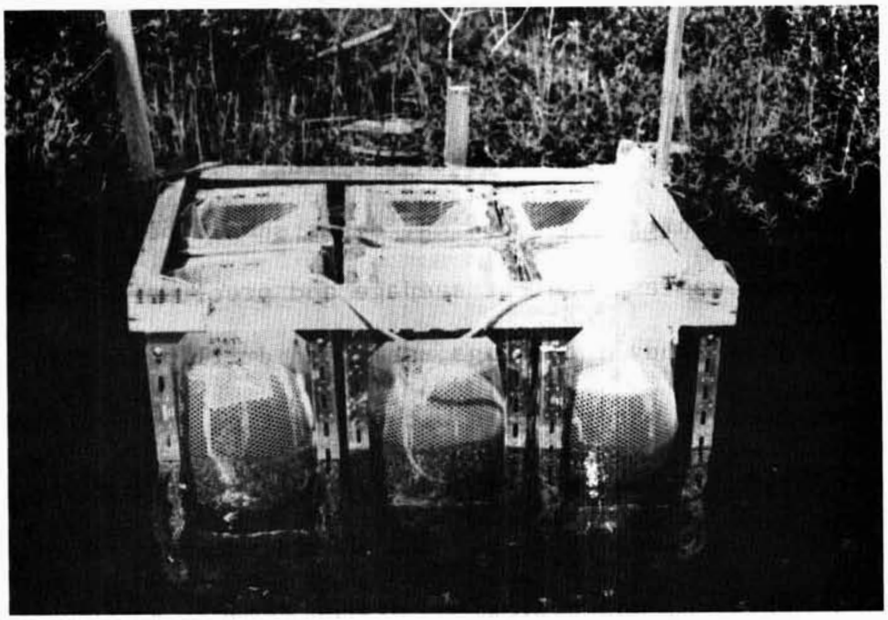

Photo 1. Apparatus used for conducting field bioassays.

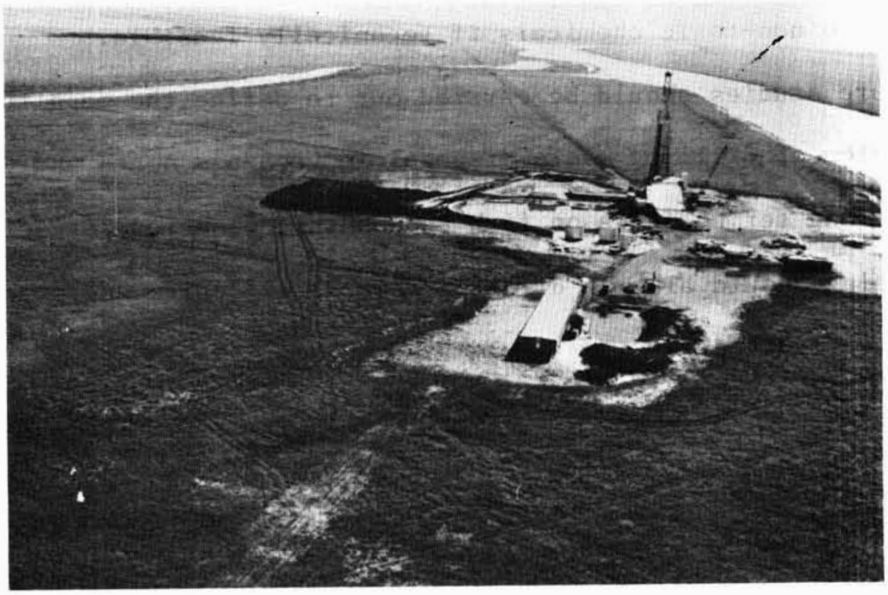

Photo 2. Imperial Oil Rig 51 location on Richards Island after flooding.

Photo 3. Imperial Oil Rig 51 location during spring flood.

Photo 4. Imperial Oil Rig 51 sump.

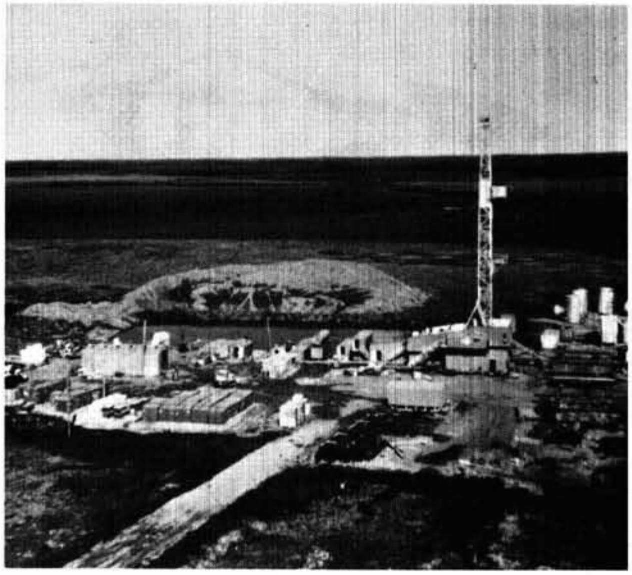

Photo 5. Gulf Oil Rig 15 location north of Parsons Lake.

Photo 6. Aerial view of Gulf Oil Rig 15 sump.

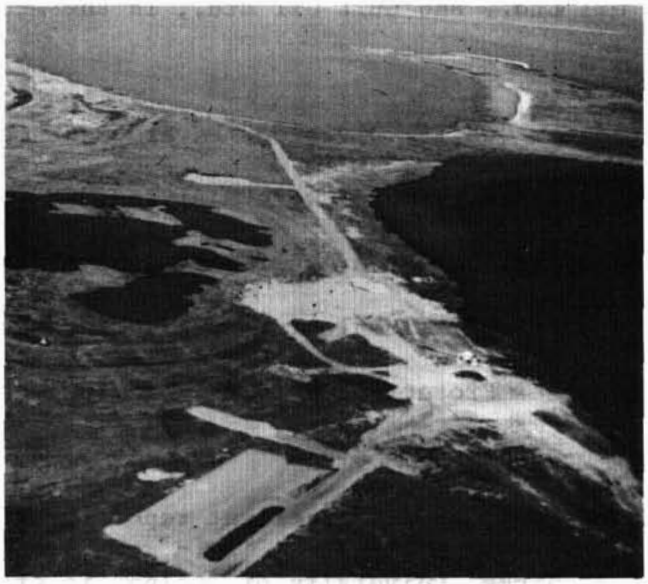

Photo 7. Example of a scar left on the tundra upon completion of a drilling operation.

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The Department is grateful for the cooperation and assistance provided by the Arctic Petroleum Operators Association, Edmonton: in particular Mr. J. Goldburn, Imperial Oil Ltd., Mr. E. Locusta, Gulf Oil Ltd., and Mr. F. Wilkin, Shell Oil Ltd., who made chemicals available for testing and supplied basic information. Logistic support and accommodation by Imperial Oil Ltd., and Gulf Oil Ltd,, in the Mackenzie delta area is much appreciated.

Mr. P. Fee, Water Quality Division, Environment Canada, Calgary ensured that water and sediment samples were analysed. Mr. D. Shaw, Energy Resources Conservation Board, Edmonton, performed laboratory analysis of sump fluid samples and provided valuable information through his experience. Mr. V. Chacko, Environmental Protection Service, Winnipeg carried out supplementary analysis on sump samples.

The advice, cooperation and excellent report provided by Dr. J. Sprague, W. Logan and B. Hicks, University of Guelph, is gratefully acknowledged.

Special thanks are due to Mr. John Hunt, Fisheries Officer, Inuvik and Mr. Andrew Didiuk, Summer Assistant. Without their help much of the field study would not have been possible.

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APPENDIX

ACUTE LETHAL TOXICITY TO TROUT
OF DRILLING FLUIDS AND THEIR CONSTITUENT CHEMICALS
AS USED IN THE NORTHWEST TERRITORIES

ACUTE LETHAL TOXICITY TO TROUT OF DRILLING FLUIDS AND THEIR CONSTITUTENT CHEMICALS AS USED IN THE NORTHWEST TERRITORIES

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Under a contract issued by:

RESOURCE DEVELOPMENT BRANCH

FISHERIES SERVICE (CENTRAL REGION)

CANADA DEPARTMENT OF THE ENVIRONMENT.

April 30, 1973.

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PART I

General Conclusions and Recommendations

(1) Three drilling fluids were tested. They killed fish in a few days at concentrations from 0.83% to 5.3%. It is possible that other drilling fluids might contain higher concentrations of acutely toxic components.

(2) In this report we deal only with the acute toxicity of materials dissolved or dispersed in the testwater. The settling of suspended solids could further damage aquatic organisms in their natural habitats. If drilling fluids were spilled, settling solids could "blanket out" the invertebrate food organisms, or clog spawning grounds of fish. These effects should be evaluated in laboratory and field tests.

(3) Possible effects on aquatic birds, of spilled drilling fluids and their components, are not covered in this study. They should be given at least preliminary evaluation.

(4) Twenty-seven common components of drilling fluids were tested for their individual toxicity. Their lethal concentrations ranged over four orders of magnitude (see item 11). The use of the more dangerous ones should desirably be discontinued and non-toxic substitutes should be found.

(5) The toxicity of simulated whole drilling fluids, made up in the laboratory, should be tested. The objectives would be to determine whether the toxicity of the more dangerous components would come through undiminished in the mixture, and whether individual toxicities would add on to each other. It would seem that they might; see item (13).

Summary of Specific Findings

(6) Most of the results given in this report are based on static bioassays with small rainbow trout, carried out in our laboratory. Test temperature was 10.5°C (51°F) and the water was hard. In a few cases of common or well-known materials, the information on toxicity has been derived from a review of the literature, and these cases are indicated in the body of this report.

(7) Three whole drilling fluids, shipped from sites in the N.W.T., were tested. A sample from Imperial Rig 51 had a threshold lethal concentration (LC50) of 0.83% (with 95% confidence limits of 0.71% and 0.96%). A later sample from Imperial Rig 51 had a threshold LC50 of 5.3% (3.7 and 7.6% limits), and one from Gulf Rig 15 had a threshold LC50 between 3.2% and 5.6% with an informal estimated LC50 of 4.2%.

(8) Drilling fluids may change their characteristics considerably, as might be expected. The LC50 for fluid from Rig 51 changed by a factor of six from July to September. Suspended solids settled much more quickly in the July sample. It also had a high pH, which was less extreme in the September sample.

(9) Suspended solids (S.S.) in drilling fluids settled rapidly. In one fluid, S.S. were about 130% on a weight/volume (kg/ℓ) basis, at zero time after thorough mixing. However, settling reduced this to an estimated 33% in about 2 minutes. Two other fluids had similar S.S. of 38% and 43% after about 2 minutes settling. S.S. further decreased by one order of magnitude during periods ranging from half-a-day to 10 days, depending on the fluid, even though the tanks contained a submerged mixing pump.

(10) Suspended solids may account for some of the direct lethal action of drilling fluids at higher concentrations. However poisonous components are probably the main active agents at concentrations near the 96-hour LC50. Further specifically-designed experiments are needed to determine this with certainty.

(11) For the individual chemical constitutents, the table below gives 96-hour LC50's in milligrams per litre or microlitres per litre (=approximately p.p.m.) according to whether the material is solid or liquid. The order of listing is from least toxic to most toxic. The 95% confidence limits are given in parentheses.

Threshold LC50 above 10,000 p.p.m. = approximately 1% or more.

Gypsum (Plaster of Paris)	>56,000
Bentonite	>10,000
CMC - Regular	>10,000
CMC - Hi Vis	>10,000
Calcium chloride	>10,500
Aluminum stearate	(Not tested. Insoluble. Toxicity from suspended solids might be similar to Bentonite or Barite)

Threshold LC50 between 1,000 and 10,000 p.p.m.

Barite	>7,500
Sodium bicarbonate	7,550
Torq-Trim	2,270 (1580,3250)
Potassium chloride (Muriate of potash)	2,020 (1920,2090)
Ferrochrome lignosulfonate	1,530 (1140,2050)

Threshold LC50 between 100 and 1,000 p.p.m.

Sodium acid pyrophosphate (S.A.P.P.)	870 (662,1140)
Potassium chromium sulphate (Chromalit)	730*(560,1000)*
Ben-Ex	665 (527,836)
Kelzan - XC	440*(320,560)*
Metso Beads	>100, <560*
Caustic (Celanese)	105 (81,136)

Threshold LC50 less than 100 p.p.m.

Capryl alcohol	83*(56,100)*
Tricron	63 (46,87)
Paraformaldehyde	60 (46,78)
Skot-Free	52 (36,76)
Swift's Rig Wash	22 (11,42)
B-Free (10-day LC50)	7.5*(5.6,10)*
Dominion Rig Wash	14*(10,18)*

The following chemicals had preliminary bioassays run, but because of an insufficient supply of test-material, a definitive LC50 cannot be stated.

SS-100	>1,000
FLR-100	>1,000
Staflo	>1,000

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*In these cases, a formal probit analysis could not be run, because only 0% and 100% responses were obtained. The true value of the LC50 lies between the values given in parentheses, which in these cases are extreme limits, not 95% confidence limits. The estimate given of the LC50 is an informal one, based on approximate methods.

(12) The standard dilution water was very hard. However, toxicity of a drilling fluid was not much different in a "medium-hard" dilution water, i.e. having one-third the total hardness of the standard water.

(13) An estimate of theoretical toxicity was made, for the drilling fluids of Imperial Rig 51 and Gulf Rig 15, based on the total materials used according to the drilling logs. The theoretical toxicities, based on individual components, were 0.92% and 2.0%. These are surprisingly close to the actual measured toxicities of the fluids, 0.83% to 5.3%. Therefore, as an initial working hypothesis, it might be assumed that toxicity of the total fluid can be predicted by adding up the toxicities of the individual components. Further research might disprove this hypothesis, but for the moment it is convenient for assessing potential danger of pollution by drilling fluids. Total toxicity of a whole fluid could be estimated from the components listed in the drilling log. Highly toxic components could be considered to retain their toxicity in the whole fluid.

PART II

MATERIALS AND METHODS

Whole Drilling Fluids.

Three "grab" samples of drilling fluids were taken from sumps of exploratory Rigs in the Northwest Territories and shipped to Guelph. Two samples came from Imperial Oil's Rig 51 and another sample from Gulf Oil's Rig 15.

Upon receipt, containers were stored in a cold room at 1°C. Preliminary tests were started within a day or two, and full-scale tests were done as soon thereafter as possible, usually within a few days.

To make up test-solutions, the containers were opened and the contents agitated to re-homogenize the liquid. The required amount of drilling fluid was measured out volumetrically and poured into the test tank. Dilution water was added to make up the total volume for the particular concentration desired. The test-solution was then stirred until homogeneous.

Constituent Chemical Components.

All of the chemicals tested are used in water-based drilling mud systems. These are suspensions of clays and other solids in water (Collins 1971). The functions of the chemicals are described in the table below according to a classification accepted by the Subcommittee on Drilling Fluids, American Association of Oilwell Drilling Contractors. The list gives only the primary use of the material, and many of them have other uses. For simplicity, the full description of all uses of a component is given in the RESULTS, in the section devoted to that material.

Weighting Material

Barite

Viscosifiers

Wyoming Bentonite
Ben-Ex
Kelzan-XC

Fluid Loss or Filtrate Reducers

Sodium carboxymethylcellulose (CMC)
FLR-100*
Staflo*

Thinner

Ferrochrome lignosulfonate
(Q-Broxin and Peltex)

Defoamer

Aluminum stearate

Calcium Remover

Sodium bicarbonate

Shale Control Inhibitor

Gypsum (Plaster of Paris)
SS-100*

Corrosion Control

Metso Beads*

pH Control

Calcium chloride
Caustic (Celanese)

Bactericide

Paraformaldehyde

Dispersants and Surface-active Agents

Sodium acid pyrophosphate
(S.A.P.P.)
Torq-Trim
Skot-Free
Tricron
B-Free*
Swift's Rig Wash
Dominion Rig Wash

Function not known by us

Capryl alcohol
Potassium chromium sulphate
(Chromalit)
Potassium chloride
(Muriate of potash)

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*The components marked by an asterisk were donated by Shell Canada Limited and supplied by International Drilling Fluids. In addition to these chemicals, Shell indicated that it was planning to employ Potassium chloride, Sodium hydroxide, Sodium carbonate, Bentonite and Barite. All other components were donated by Imperial Oil Limited and supplied by Baroid of Canada Limited.

Preparation of Component Chemicals for Testing.

A small amount of the chemical to be tested was placed in a 1-litre Erlenmeyer flask which had been filled previously with water. The flask was shaken then set aside for an hour. This indicated the physical reaction of the chemical in water. Depending on that reaction, the chemical was then prepared for bioassay by one or other of the following methods:

For liquids miscible in water, the chemical was measured out by volume and added to the required amount of dilution water. The test solution was gently stirred to mix it thoroughly.

For solids which were soluble in water, the chemical was weighed out, added to the dilution water, and the test solution stirred to mix thoroughly.

For solids forming colloids or suspensions in water, the required amount of chemical was weighed out and then added slowly to a running blender which had been filled previously with dilution water. The blender was run for 2 to 3 minutes after the last of the chemical had been added. The resulting emulsion was poured into dilution water in the test tank, and gently stirred to mix.

Test Fish and Holding Conditions.

Rainbow trout (*Salmo gairdneri* Richardson) were used in these tests. They were a specific pathogen free strain obtained from Shamrock Springs Hatchery, Erin, Ontario.* Their initial length was 2.5 to 4.0 cms, and exact sizes of the groups used in the tests are given in Appendix B. The fish were subjected to at least ten days of holding and acclimation before being used in tests, and usually much longer than that. An overall mortality of 8.7% was recorded, mostly during the initial phases of acclimation, and mortality was satisfactorily low before the tests were started, by the usual criteria (Sprague,1969).

The fish were held in cylindrical dark green fiberglass tanks with smooth interiors and a central bottom-draining standpipe outlet. Tanks were filled to a depth of about 20 cm. A continuous inflow of new water gave a 90% replacement time of about 1½ hours, for water in the tank. Fish were fed a maintenance diet of 1% of body weight per day of commercial fish food granules. They were held under a photoperiod of 14 hours of "daylight" provided by incandescent bulbs, with a half-hour of gradual increase or decrease of light intensity at either end.

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*Mailing address: Erin Conservation Holdings, Box 1021,
Guelph, Ontario.

The water supply used for holding and testing was natural water from a drilled well. It was thoroughly aerated before use, and brought to the correct temperature as necessary, with non-toxic heat-exchange elements. The water used for holding was hard, with a hardness of 353 ± 10 mg/ℓ as $CaCO_3$. Temperatures in the holding tanks were 10.5 ± 1.0°C, dissolved oxygen was always within 5% of saturation, and the average of all pH readings was pH8, with a range of 7.6 to 8.5.

Test Conditions and Procedures

The general methods, procedures and calculations followed for measuring the toxicity of the chemicals was that outlined by Sprague (1969) and subsequently refined in a later publication (Sprague, In press). Static tests were done. That is, a given concentration of test-mixture was made up and not renewed during the 4-day test. (Some drilling fluids were renewed at 2 and 4 days.)

Test-tanks were circular enamelled washing machine tubs containing from 30 to 60 litres of water depending on the size of the fish. The average weight of the fish in the preliminary bioassay was used in calculating the required test volumes. Based upon this weight it was endeavoured to have a volume of 3 litres, and in all cases at least 2 litres, per gram of fish per test-day. The exact amounts of water, and relation to weights of fish, are given in Appendix B.

To prevent a carry-over of chemical from one test to another, the test tanks were washed between tests using Wescodyne, 37% Formalin, and then rinsed several times with clean water.

If for reasons of turbidity or opaqueness, the fish could not be observed in the tank, a "basket" of stiff nylon screening was placed in the tank. The basket was raised to observe the fish at the observation times. If the waste contained settling solids, a net basket and a submersible circulating pump were added to each tank. This helped prevent the solids from settling and moved the water around the tank. The surface velocities of water measured in tanks with pumps was 6 cm/sec. at a distance of 10 cm from the side of the tank, the normal location selected by the fish.

Incandescent lights were installed 50 cm above the water level in the test tank and the light intensity at the water surface was about 180 lux.

Test-water was the same well-water as used for holding the fish. In one case this was softened by using deionized water to see if this made any difference in the results.

Detailed chemical analyses during the tests are reported in Appendix B, but some general statements may be made here. Water hardness was measured prior to the introduction of the chemical, one hour after initiation of the test and daily thereafter by the Hach method. In general it was found to be 300 to 360 mg/ℓ.

Temperature was kept constant in the test tanks by immersing them in a constant-temperature water bath, the water of which was recirculated through a cooling apparatus. Temperatures of the bath and test tanks were taken prior to the introduction of the chemical, one hour after initiation of the test and daily thereafter, using a standardized mercury thermometer.

Test temperatures were in the range $10.5^{\circ}C \pm 1$ and the average for each material tested is given in Appendix B. Detailed reporting of temperatures seems unnecessary and has not been done. However, as a typical example, one set of tests for a drilling fluid had an average of 10.2° for all observed temperatures. The range of individual temperatures was from 9.4 to 10.8. Average temperatures in the five test-tanks were 10.5, 10.3, 10.4, 9.6, and 10.4°.

The dilution water in each test tank was aerated for 12 hours before the introduction of the chemical and the fish. Dissolved oxygen was measured prior to the introduction of the chemical, one hour after initiation of the test and daily thereafter by the Winkler method. The initial values were 85% of saturation or more.

The hydrogen-ion concentration was measured on the same schedule as temperature and oxygen, using a Fisher pH meter and the Hach method.

Suspended solids were measured in the tests with whole drilling fluids. This was done by passing a representative aliquot through a 0.45μ Millipore filter. The results were expressed in the standard way, as mg. of dried solids per litre of sample.

Preliminary or ranging bioassays.

These were done at concentrations ranging over three orders of magnitude (at 10, 100, 1000 and 10,000 or at 1, 10, 100 and 1000 mg/ℓ or μℓ/ℓ). These tests were not done in enamelled tubs but in polyvinyl tanks containing 15 litres of water. After aeration and the addition of the chemical under test, two rainbow trout were added to initiate the bioassay. Observations were made at appropriate time intervals. These preliminary tests were merely to orientate the following definitive bioassays, and the results (with four exceptions) were not used in this report.

Definitive bioassays.

Upon completion of the preliminary bioassays, the definitive bioassays were run. The concentrations to be tested were between the concentration which gave 100% survival and the concentration which gave 100% mortality. The concentrations were selected from the logarithmic series of 1.0, 1.8, 3.2 , 5.6, and 10, or multiples of ten thereof. After aeration and the addition of the chemical under test, five rainbow trout were added to initiate the bioassay. Exposures were continuous for at least 96 hours, and were as long as ten days for some tests with whole drilling fluids. Observations of mortality were at 15 minutes, 30 minutes, 1 hour, 2 hours, 4 hours, 8 hours, 14 hours and twice daily thereafter.

Calculations of Results

The median effective time (ET50) was estimated for each concentration, as the tests were underway. This was done by plotting on log-probit paper according to the methods of Litchfield (1949). The 95% confidence limits of the ET50 were also estimated by these methods.

A toxicity curve was constructed as the tests proceeded, using the ET50's. These are shown for each chemical or fluid in the Results. In most cases the toxicity curve showed that the tests could be stopped at 96 hours, since this seemed equivalent to the threshold LC50 (i.e. additional mortality had stopped by 96 hours).

The 96-hour LC50 and its confidence limits was estimated by use of the computer and checked for reasonableness by plotting on log-probit paper. The computer program was PROBITANAL, program 199 PROBIT of the Institute of Computer Science, University of Guelph. It is based on the standard iterative method of Finney (1952).

An <u>informal estimate of the LC50</u> was necessary in some cases where the fish gave very sharp "all-or-none" responses. No partial mortalities were obtained in the various test-concentrations, only 0% and 100% mortalities. Finney's method of probit analysis does not apply in such a situation and therefore there could be no formal estimate of the LC50 and its confidence limits. The only thing which was known with exactness was that the true value of the LC50 was between the highest concentration which caused no mortality, and the lowest concentration which caused complete mortality. (In most such cases in this study, these two concentrations were close and there was little doubt about the approximate value of the LC50.) Informal estimates of the LC50 have been provided in these cases by an approximate method. The value of 2% mortality was substituted for the 0%, and 98% was substituted for the 100%. This was done in the computer program and in the graph used for checking reasonableness. This situation applied for Rig 15 drilling fluid, and for six components as indicated in the Summary and in the Results.

RESULTS FOR WHOLE DRILLING FLUIDS

The main results are given here in the body of the report. Details have been given in the appendices. Appendix A gives for each concentration tested, the percentage mortality, and the median survival-time with the slope factor for its associated probit line. Appendix B gives various background information such as when the test was done, temperature and pH, size of fish and volume of testwater.

Imperial Oil Rig 51 (July)

The 96-hour LC50 was 0.83% by volume (8,300 $\mu\ell/\ell$). The 95% confidence limits were 0.71 and 0.96% and the slope of the probit line was 13.80. The toxicity curve was a very standard and uncomplicated one (Fig. 1). The lethal threshold concentration was evident in about 15 hours, and was the same as the 96-hour LC50. The 8 -day LC50 was 0.80, not significantly different from the 96-hour value.

This sample was alkaline, causing a maximum of pH 9.95 in very strong mixtures (Fig. 2). It is possible that values above pH 9.5 would cause direct acute toxicity to the trout, given fairly long exposure, but it is unlikely that lower values would do so.

It seems that lethal effects are not only from pH, nor only from suspended solids (see below) but are also from one or more poisonous compounds present in this waste. For example, it is clear that pH 8.85 is not lethal to fish, since this pH would prevail (Fig. 2) at a non-lethal concentration of 0.6% of the waste. Yet in hard water, at the same pH, caused by 3.2% concentration of waste, fish died quickly, in 6 hours. It is doubtful if suspended solids *per se* were lethal (Fig. 3). It seems to have been a toxic chemical causing the rapid death.

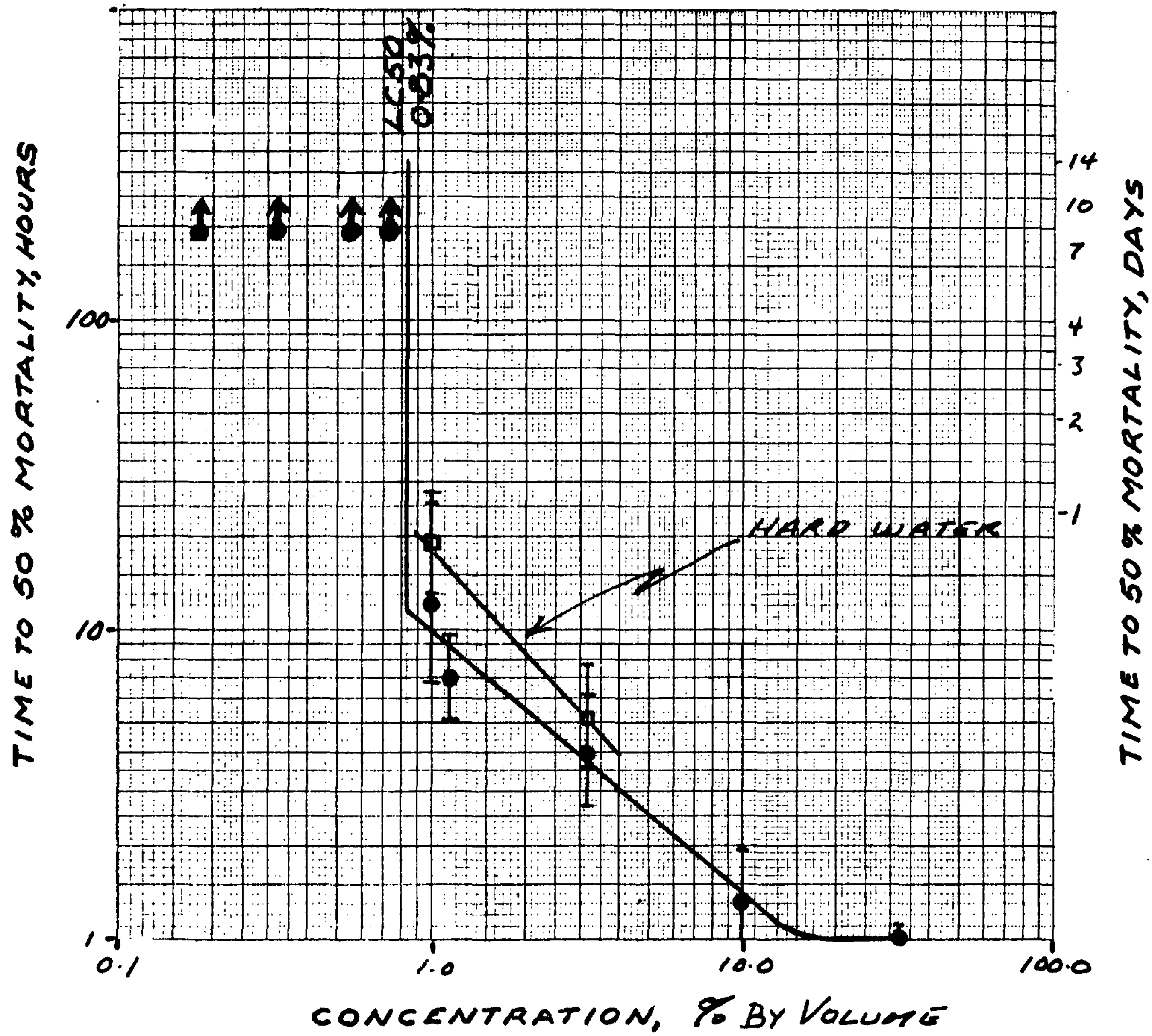

Fig. 1. The toxicity curve for drilling fluid from Rig 51, collected in July, and tested against rainbow trout. Most of the tests were run in medium-hard water (120 mg/ℓ as $CaCO_3$). Two values were obtained with very hard dilution water 353 mg/ℓ as $CaCO_3$), which was standard in other tests with drilling fluids and components. The LC50 is the one described in the text, as calculated by the standard procedure.

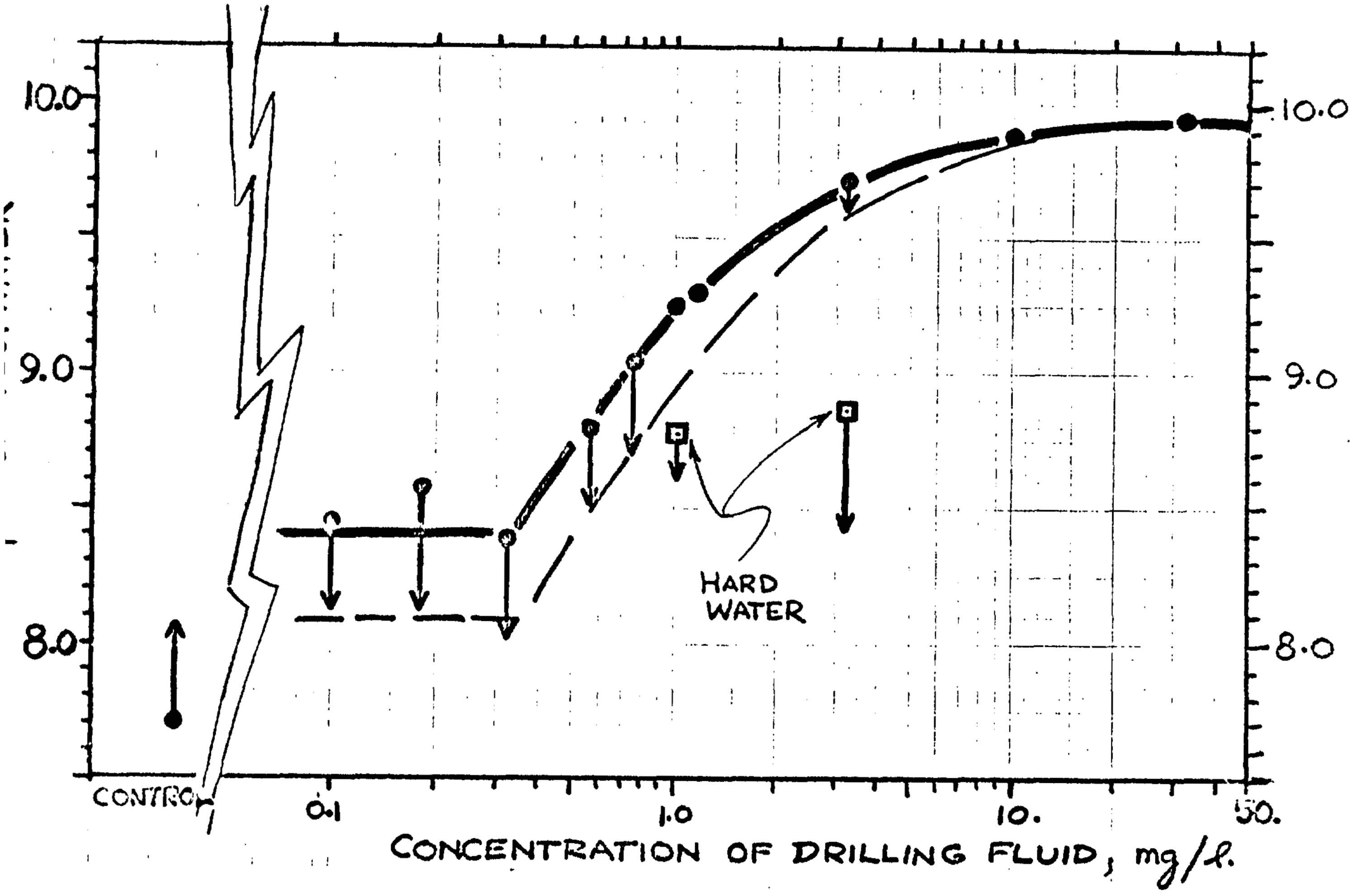

Fig. 6. Rise in pH of testwater caused by drilling fluid from Imperial Rig 51 in July. Round points are initial concentrations, arrows indicate final concentration at the end of the test, which was 4 days after the last change of test-water for the lower concentrations. Square points are two tests in very hard water (353 mg/ℓ hardness) compared to the usual medium-hard water (120 mg/ℓ) used in most tests with this particular fluid.

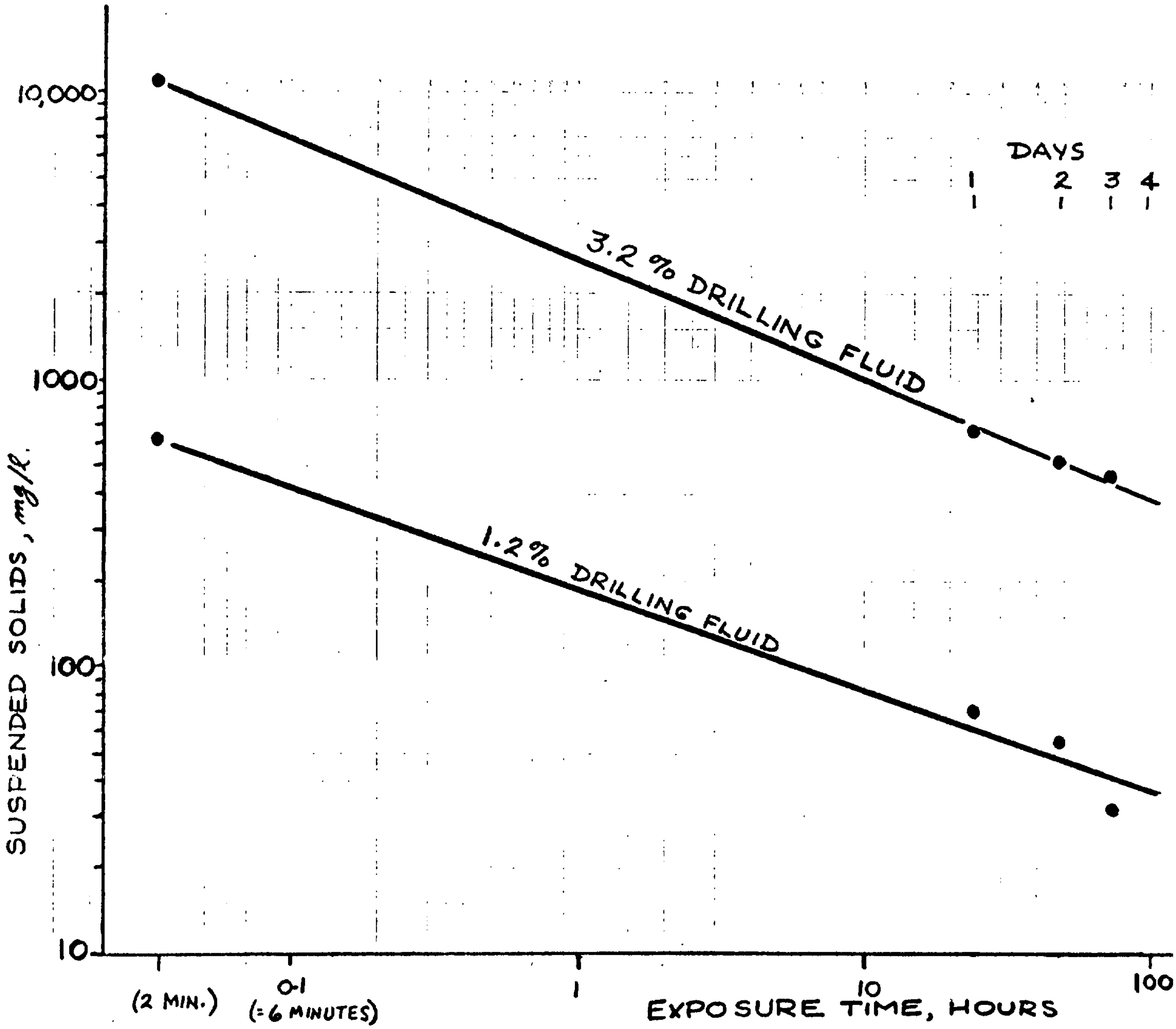

Fig. 3. Decline in suspended solids in test tanks, for sample of waste from Imperial Oil Rig 51 in July.

Water hardness has only a very small effect on toxicity. Most of the tests were done using medium-hard dilution water (120 mg/ℓ as $CaCO_3$) made up by diluting the standard very hard (353 mg/ℓ) ground water with de-ionized water. In very hard water fish survived somewhat longer than in the medium-hard dilution water (Fig. 1), but the differences were not statistically significant. Probably the effect on lethal threshold would be very small or none.

The very hard water buffered the pH effect of the wastes, and this may account for the small differences in survival-times.

Suspended solids in raw waste at zero time were 1,300,000 mg/ℓ, (130% on a weight/volume basis) which is a specific gravity of 1.3. An estimate of S.S. in raw waste after 2 minutes settling, based on 2-minute value of S.S. in a test-tank of 3.2% concentration, showed 330,000 mg/ℓ or 33% weight/volume. This is similar to the 38% and 43% estimated for the other two drilling fluids described below. It is evident that a lot of heavy particles settle out immediately in the test-tanks, despite the presence of a circulating pump. S.S. settled to about one-twentieth of the 2-minute value, in a 3-day period, and had decreased by a factor of 10, in half a day.

There is a discrepancy in the amounts of S.S. found in the test-tanks and shown in Fig. 3. The higher concentration has at least ten times more S.S. than the lower one, whereas we would expect only 2.7 times as much. This is no doubt because of difficulty in sampling these wastes. The lighter particles, and the active toxicants, seem to have been adequately sampled because of the regular relations in the toxicity curve. These estimates were made at an early stage in the summer program, and may not be as accurate as later estimates of S.S.

The S.S. may have been a partial cause of mortality at concentrations greater than 3.2 mg/ℓ of waste, but was probably a negligible factor at concentrations down around the threshold. In 3.2% concentration there was probably about 1500 mg/ℓ S.S. at the time of death of the median fish (4 to 5 hours). This is one to two orders of magnitude less than the usual concentrations causing acute lethality, unless the S.S. are of special shape such as extremely sharp, or fibrous.

Other details include dissolved oxygen concentrations of 6.0 to 6.2 mg/ℓ in test concentrations of 10 and 32 mg/ℓ; 8.0 to 10.4 mg/ℓ in test concentrations from 1.0 to 3.2 mg/ℓ; and 9.5 to 11 mg/ℓ in test concentrations below 1.0 mg/ℓ and in the control. It seems likely that the waste interfered with the chemical determination of oxygen, and that oxygen values were higher than measured, in the stronger dilutions of waste. Test-volumes were 1.6 litres/gram of fish per day for the first four days, which is not quite adequate. However, mortality generally occurred in the first day or not at all, so test-volume was more than adequate during the important early parts of the test. All test concentrations were renewed at 96 hours, and the experiments then ran for a further four days for a total of 8 days.

Imperial Oil Rig 51 (September)

The 96-hour LC50 was 5.3% by volume (53,000 μℓ/ℓ). The 95% confidence limits were 3.7 and 7.6%. The slope of the probit line was 4.97. Only the critical concentrations near the threshold were tested, resulting in an apparently simple toxicity curve (Fig.4). The lethal threshold concentration was almost certainly the same as the 96-hour LC50, since no additional fish died during the subsequent exposure of 10 days in 5.66% fluid.

Suspended Solids (S.S.) themselves might be responsible for mortality but this cannot be decided without further tests. There are several thousand mg/ℓ of S.S. in dilutions near the lethal threshold, and this much could be acutely toxic. However, it is not warranted to make too much speculation on this point, since toxicity of S.S. depends so much on size and shape of the particles. Experiments could be devised to determine if mortality is caused by poisonous materials or simply by the physical effect of S.S.

Suspended solids were measured frequently as shown in Fig. 5. The S.S. in raw drilling fluid may be estimated by back-calculation from the initial solids content of the five test-concentrations, 4 of which were renewed once, thus giving a total of 9 estimates. The estimates, in thousands of mg/ℓ, are 479, 332 and 563, 579 and 498, 271 and 236, and 478 and 462. The average of these is 433,000 mg/ℓ or 43.3% as weight/volume. This figure, after two minutes settling, could be compared with field values.

Overall, the picture in Figure 5 is reasonably consistent. A dilution of 1% had about 5,000 mg/ℓ S.S. at the start, and by five to ten days had declined to about 500 mg/ℓ. A dilution of 10% was initially just one order of magnitude higher, as it should be, and the decline was parallel on the logarithmic plot. Other concentrations were in between in a fairly regular pattern. The only

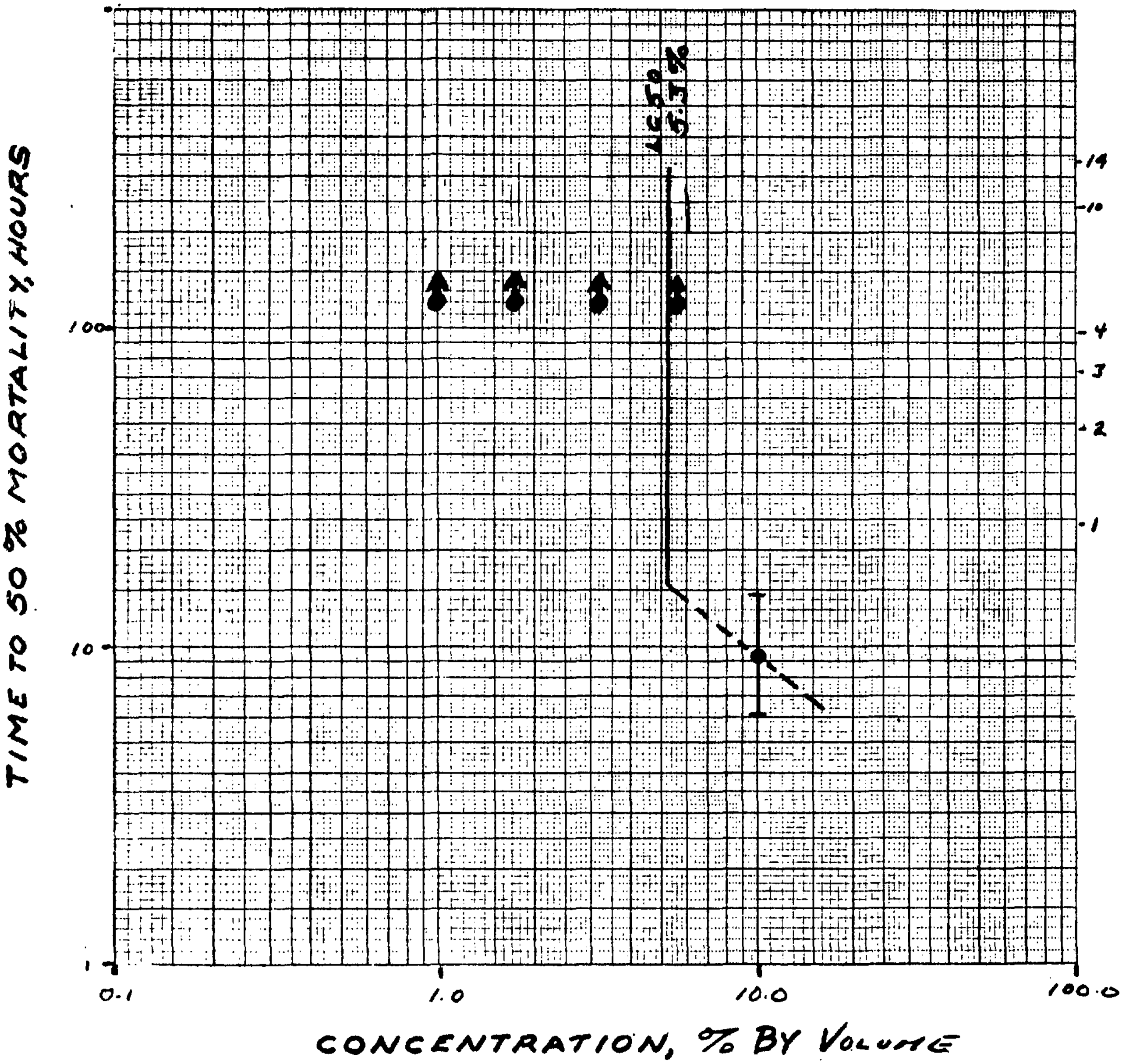

Fig. 4. Toxicity curve for drilling fluid from Imperial Oil Rig 51, in September, tested against rainbow trout.

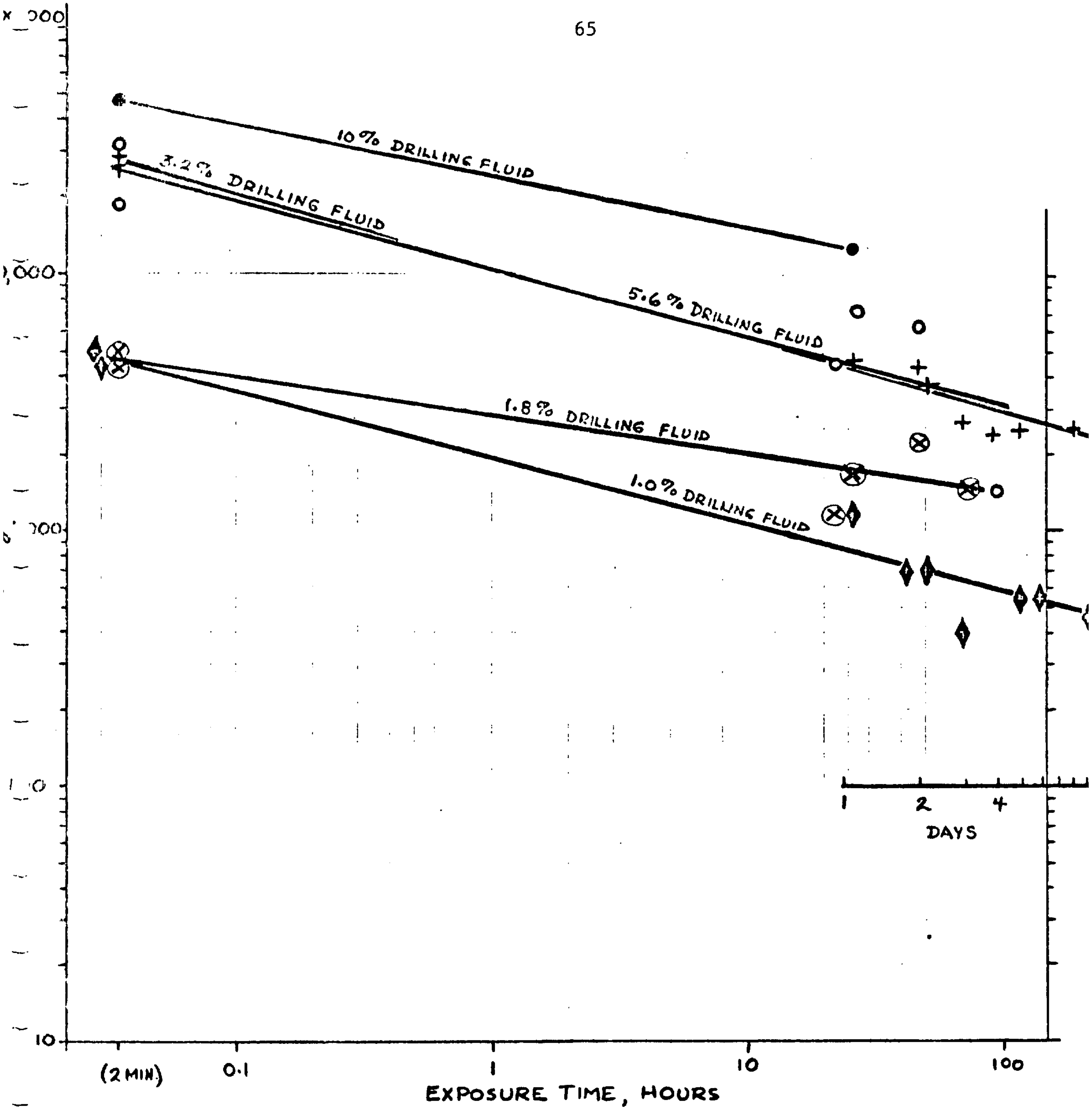

Fig. 5. Decline in suspended solids in test tanks containing various dilutions of drilling fluid from Imperial Oil Rig 51 in September. Initial sampling was attempted immediately after the test-mixture (or renewal of the test-mixture) was made up, but has been arbitrarily placed at 2 minutes on the time scale. A submerged pump in the tank agitated the test mixture as described in text.

exception is that S.S. are somewhat higher than might be expected in the 3.2% dilution of Rig 51 (no mistake in calculations was evident). There are, of course, difficulties in sampling such a heavy suspension of particles, many of which are rapidly sinking while one attempts to sample.

Other details of the tests were regular. There was no problem of high pH. Average pH values in the five tanks, from strong to weak concentration, were 8.95, 8.6, 8.7, 8.5, and 8.6. The probit lines were not unusual in any respect. At first glance it may seem peculiar that the lethal threshold is at a slightly lower concentration than one which killed only 40% of the fish. However this is merely an artifact of the few tests and small number of fish in each. The estimate of the LC50 is the best one, as determined by both the computer program and the probit graph, and this is shown by the reasonable confidence limits. In fact, since the test concentration of 5.66% is extremely close to the LC50 of 5.3%, it is reassuring that about half the fish died at that concentration. Test-water was changed at 48 hours and not after that. Up until 5 days of total exposure, conditions in the test tank were adequate or better, and the test was considered terminated at that time. The 96-hour LC50 is a dependable criterion of acute toxicity, and the threshold LC50 is almost certainly the same. This fluid was shipped from Inuvik on September 6 or earlier and received September 10.

Comparison of July and September samples.

The characteristics of the fluid changed considerably in the two months between receipt of the July sample and receipt of the September sample from Rig 51. Toxicity decreased from 0.83% to 5.3%. The earlier sample raised pH of the testwater but the later sample did not. The suspended solids were also different. At 3.2% concentration, the amount of S.S. in the earlier sample was similar to amounts in the two other fluids, but they dropped out much more quickly, down to about 500 mg/ℓ in 3 days, compared to 3500 mg/ℓ in Rig 51 in September.

The major lesson here is that grab samples of drilling fluids may differ in toxicity. This might be expected from the day-to-day variation in use of components. The greater toxicity of the July sample is without much doubt, caused by the added toxic action of pH resulting from the caustic soda not being neutralized. Caustic contributes a high proportion of the theoretical toxicity if not neutralized (see Discussion).

Gulf Oil Rig 15

The 96-hour LC50 lies between 3.2% and 5.6%. An informal estimate of the LC50 is 4.2% and this must be close to its true value, because of the narrow limits. The toxicity curve (Fig. 6) appears to be regular with a sharp cut-off at the 96-hour LC50 below which the fish survived for the 7-day experimental period. Therefore the lethal threshold concentration was the same as the 96-hour LC50.

It is possible that in this fluid also, an appreciable part of the toxicity resulted from suspended solids rather than dissolved toxicants. The S.S. in Rig 15 fluid were superficially similar to those of Rig 51. Estimated S.S. in raw fluid at 2 min. averaged 0.375 kg/ℓ or 37.5%. S.S. in the test tanks were initially 9,000 to 40,000 mg/ℓ, and ended in the range 1,000 to 10,000 mg/ℓ in 1 to 4 days (Fig. 7). These dilutions show a very similar pattern to the S.S. in similar dilutions of Rig 51, and a similar rate of settling.

Other details of the experiment were fairly standard. The probit lines were straight, regular, and there was little scatter of the points. Test volumes were 2.3 litres per gram of fish per day which is favourable. Testwater was renewed at 96 hours, then not changed until the tests ended at 168 hours. Since that is only 3 days beyond the change, conditions were adequate throughout the test. Hydrogen-ion concentrations were satisfactory. The initial and final values were pH 8.75 and 8.7 in the 10% mixture, and pH 8.5 and 8.4 in both the 5.6% and 3.2% mixtures. The strong testwater was somewhat elevated above the natural pH of the water, but not enough to cause any direct harm to the fish. Initial and final values of dissolved oxygen were 7.2 and 7.1 mg/ℓ in the strongest test-concentration, and 9.0 to 7.4 mg/ℓ in the other tests. These levels are quite adequate, but nevertheless it is difficult to see why they were so much lower than the saturation value of 11.3 mg/ℓ. Probably the drilling fluid interfered with the chemical test for oxygen, and levels were really higher than this. The fluid was shipped from Inuvik in early August and received on August 15.

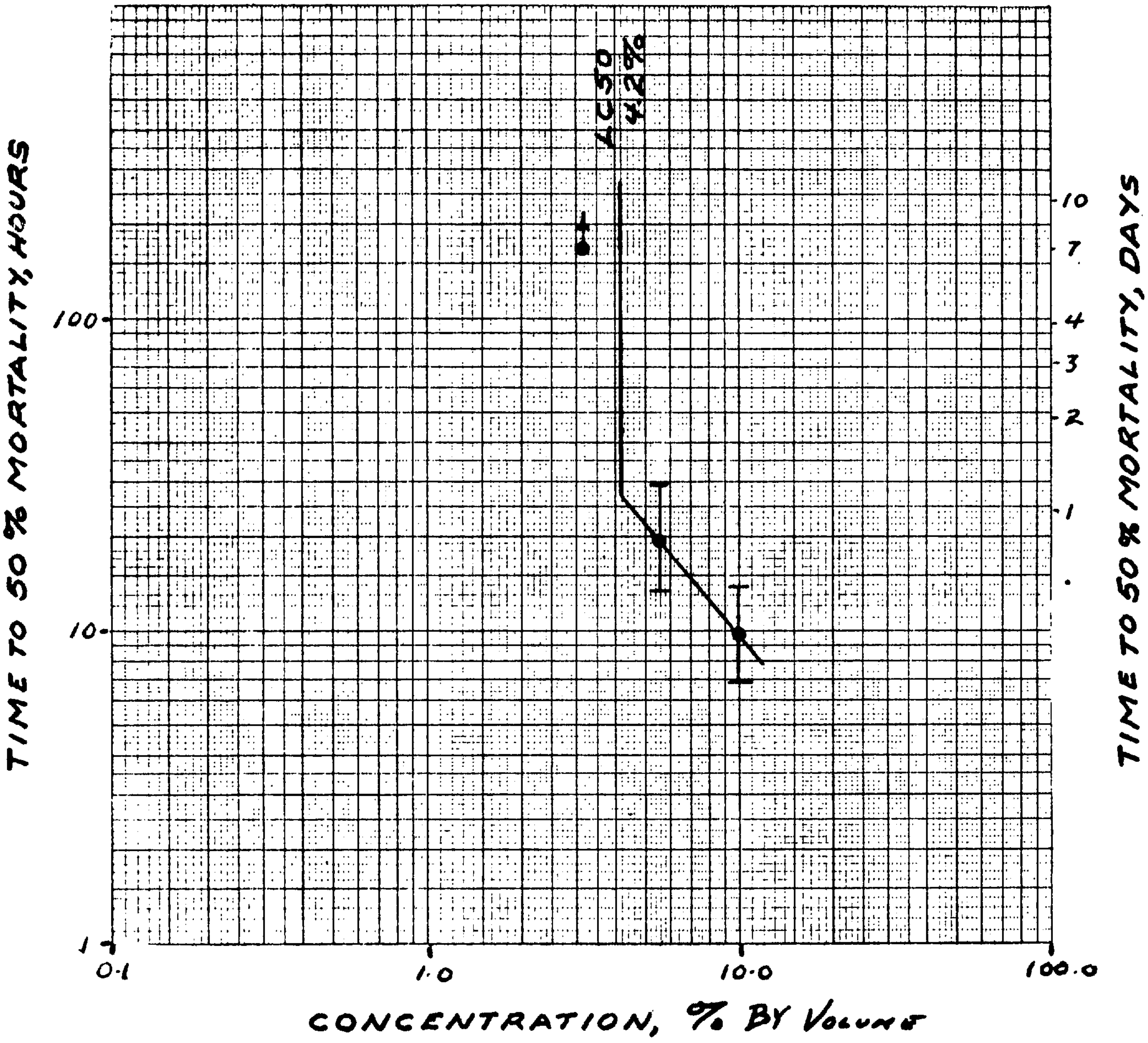

Fig. 6 . Toxicity curve for drilling fluid from Gulf Oil Rig 15, tested against rainbow trout.

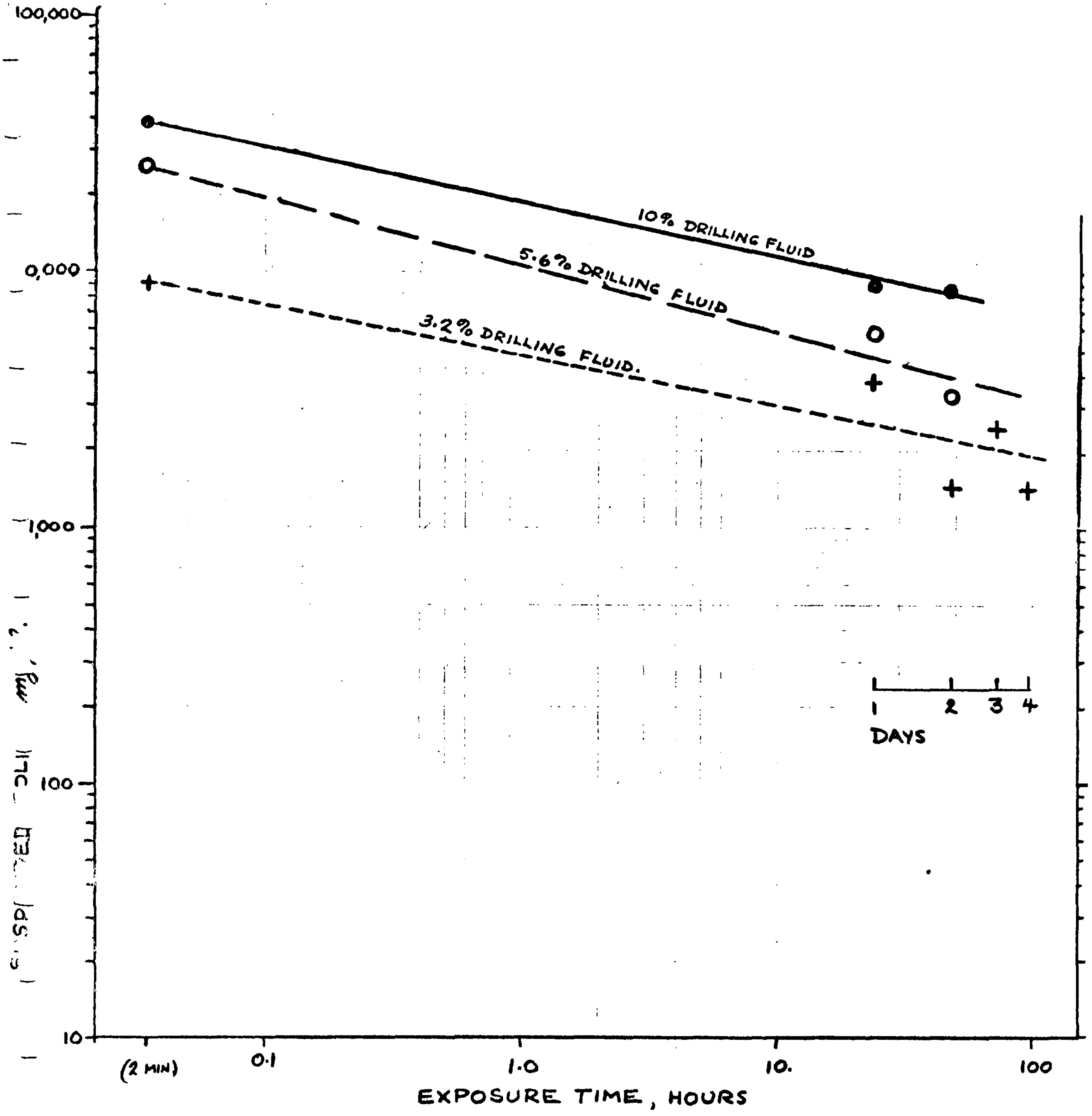

Fig. 7 . Decline in suspended solids in test tanks containing various concentrations of drilling fluid from Gulf Oil Rig 15. Other information as in Fig. DF 2.

RESULTS FOR COMPONENTS OF DRILLING FLUIDS

Gypsum (Plaster of Paris)

Gypsum is used primarily as a shale control inhibitor and also as a flocculant and calcium source.

This chemical is known generically as **calcium** sulphate ($CaSO_4.2H_2O$). When it is partially dehydrated it forms Plaster of Paris ($2CaSO_4.H_2O$) which reverts to Gypsum in the presence of water.

It was received but not tested because its low toxicity is well documented. Wallen (1957) used Gambusia affinis as a test animal. Water used as the test solution had a pH of 7.8 to 8.3, a temperature of 20^{o} to 22^{o}C and a hardness of 100 expressed as mg/ℓ $CaCO_3$. He found after 96 hours that the LC50 was greater than 56,000 mg/ℓ.

Wyoming Bentonite

This material is used primarily as a viscosifier or gel, secondarily as a filtrate or fluid loss reducer.

Neither a lethal threshold concentration nor a 96-hour LC50 was established. The clay was tested at 10,000 mg/ℓ without lethality. A blender, a circulating pump and a screen were used as described in the methods. The clay remained completely in suspension. A literature review showed no mortality of *Gambusia* at 100,000 mg/ℓ in seven days (Wallen 1951).

Sodium Carboxymethylcellulose (CMC)

This chemical, in both Regular and Hi-Vis forms, is used primarily as a filtrate reducer, and secondarily as a viscosifier. Its formula is $RnOCH_2COONa$.

Neither toxicity curve, lethal threshold concentration, nor 96-hour LC50 was established, since there was no mortality at any of the concentrations tested, even though these spanned three orders of magnitude (10, 100, 1000, and 10,000 mg/ℓ). This applied to both forms of the material, tested at these concentrations. The chemical was blended with test water before its introduction into the tank. During the test, a clear viscous layer settled on the tank bottom. The fish appeared to have no problem in sensing the presence of this dense layer. None of them swam into the layer, but all of them swam just above it.

Calcium Chloride

This chemical is used as a pH controlling additive, a shale control inhibitor and a weighting material. It may also be used as a flocculant.

A sample of the chemical, $CaCl_2$ was received but not tested. Instead the following information has been adapted from Trama (1953). The test animal was the common bluegill *(Lepomis macrochirus* Raf.). The 96-hour LC50 was 10,500 mg/ℓ. The 95% confidence limits were 9,650 and 11,300 mg/ℓ. The slope of the probit line was 13.86. As observations were taken at 24 hour intervals it was not possible to ascertain when mortality ceased. Therefore, no conclusions regarding the lethal threshold concentration can be made. In Trama's tests, a soft synthetic water Cha_{14} , was mixed with distilled water and used as the test solution. Hardness increased with each increase in chemical concentration from 6,500 to 11,900 mg/ℓ as $CaCO_3$. The pH depended on the test concentration and varied initially from 7.8 to 7.3. Since the tanks were aerated, it is assumed that the water was near saturation with oxygen.

As Trama gave observations only at 24 hour intervals, probit lines for all concentrations could not be established. The median effective time and other related data that could be ascertained was:

Conc.	ET50 (hours)	% Mort. (96 hrs.)	S	No. of Fish
12,500	22.5	100	-	10
12,000	?	85	-	10
10,800	84	60	-	10
10,500	-	40	-	10
8,700	-	20	-	10
6,500	-	0	-	10
Control	-	0	-	10

Aluminum Stearate

This chemical is used as a defoamer.

A sample of aluminum stearate ($[CH_3(CH_2)_{16}COO]_3Al$) was received but not tested. According to the Merck Index, 8th ed., it is completely insoluble in water. Therefore, it would act like a suspended or settling solid much the same as bentonite, barite and gypsum.

Barite

This is used as a weighting material.

Barite is known generically as barium sulphate, $BaSO_4$. It was not tested. Daugherty (1951) tested barite and found it non-toxic up to 7,500 ppm.

Sodium Bicarbonate

This chemical is used primarily as a calcium remover, and secondarily as a means of pH control.

Sodium bicarbonate ($NaHCO_3$) was received but not tested. Wallen (1957) reported testing sodium bicarbonate ($NaHCO_3$) with *Gambusia affinis* in a test solution of pH 7.8 to 8.3, temperature 20-22°C and a hardness of 100 mg/ℓ as $CaCO_3$. The 96-hour LC50 was found to be 7,550 mg/ℓ. This figure also appeared to be the threshold lethal concentration since mortality remained unchanged after 24 hours.

Torq-Trim

Torq-Trim is a surface wetting agent. It is composed of sulfated triglycerides plus aliphatic alcohols plus isopropyl alcohol.

The 96-hour LC50 was 2270µℓ/ℓ. The 95% confidence limits were 1580 and 3250µℓ/ℓ. The slope of the probit line was 3.99. A simple toxicity curve (Fig. 8) was produced as only concentrations near the threshold were tested. The lethal threshold concentration was not established as mortality continued up to 93 hours. All of the chemical dissolved in water.

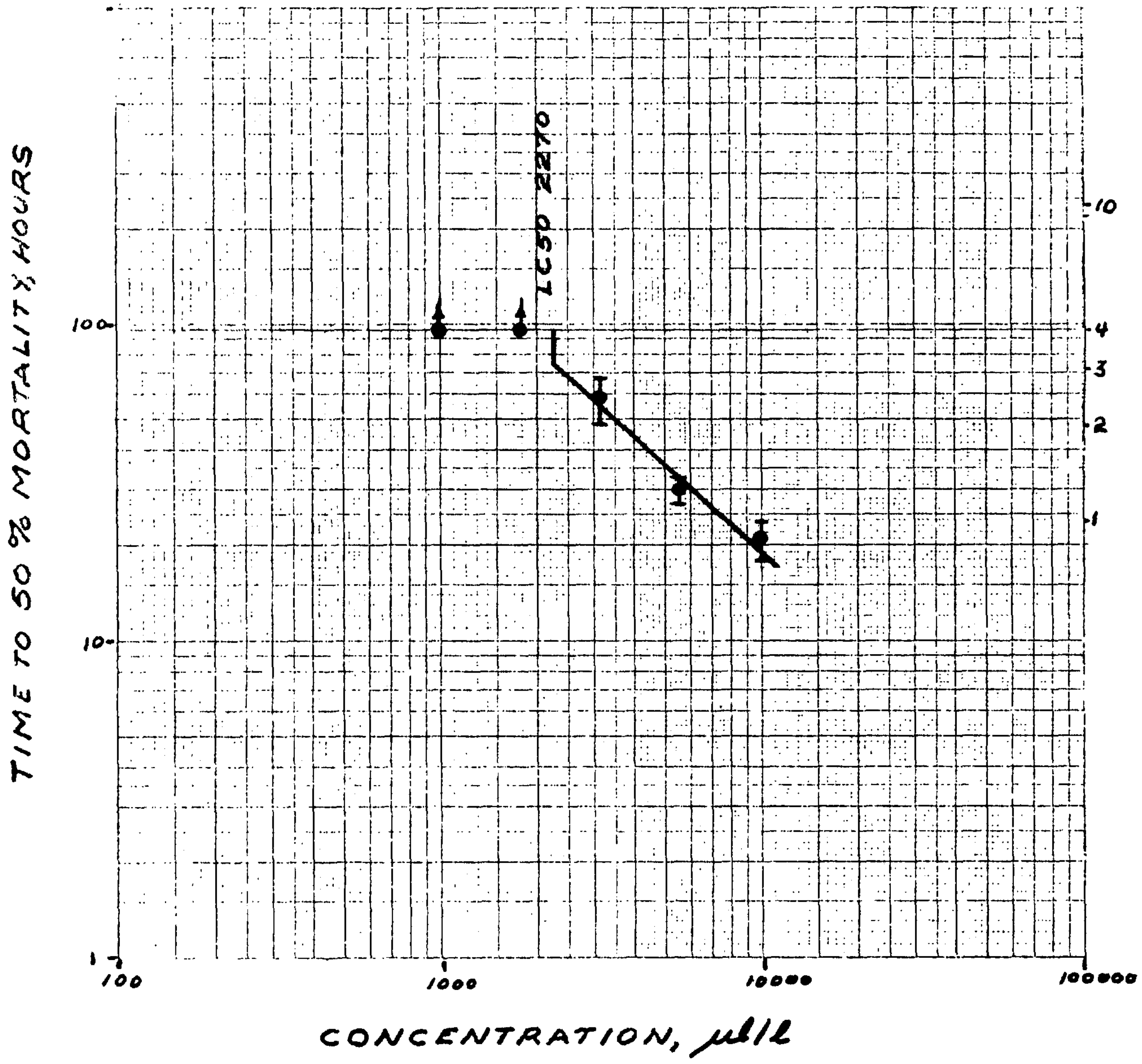

Fig. 8. Toxicity curve for Torq-Trim tested against rainbow trout.

Potassium Chloride

This chemical's function is not known to us.

Potassium chloride was received but not tested. Instead the following information has been adapted from Trama (1953), who did tests using the common bluegill. A soft synthetic water, Cha_{14} was mixed with distilled water as the test solution. Hardness was 40 mg/ℓ as $CaCO_3$. Initial pH varied from 9.37 to 8.20 then decreased to 7.25 and 7.59 by the end of the tests.

The 96-hour LC50 was 2020 mg/ℓ. The 95% confidence limits were 1920 and 2090 mg/ℓ. The slope of the probit line was 53.9. As observations were taken by Trama at 24 hour intervals it was not possible to ascertain when mortality ceased, nor could meaningful probit lines be established. The data that could be ascertained is given in the table below.

Conc.	ET50 (hours)	% Mort. (96 hrs.)	S	No. of fish
2200	-	100	-	10
2054	-	65	-	10
1911	-	10	-	10
1661	-	0	-	10
Control	-	0	-	10

Ferrochrome Lignosulfonate (Peltex or Q-Broxin)

Peltex is used as a filtrate reducer, shale control inhibitor, and as a thinner. It may also be used as an inhibitor. Q-Broxin is used primarily as a thinner and dispersant, but can be used in the same ways as Peltex.

This chemical was received under its generic or chemical name and also under the brand names Peltex and Q-Broxin. All three samples were tested and all three followed the same pattern in the bioassays.

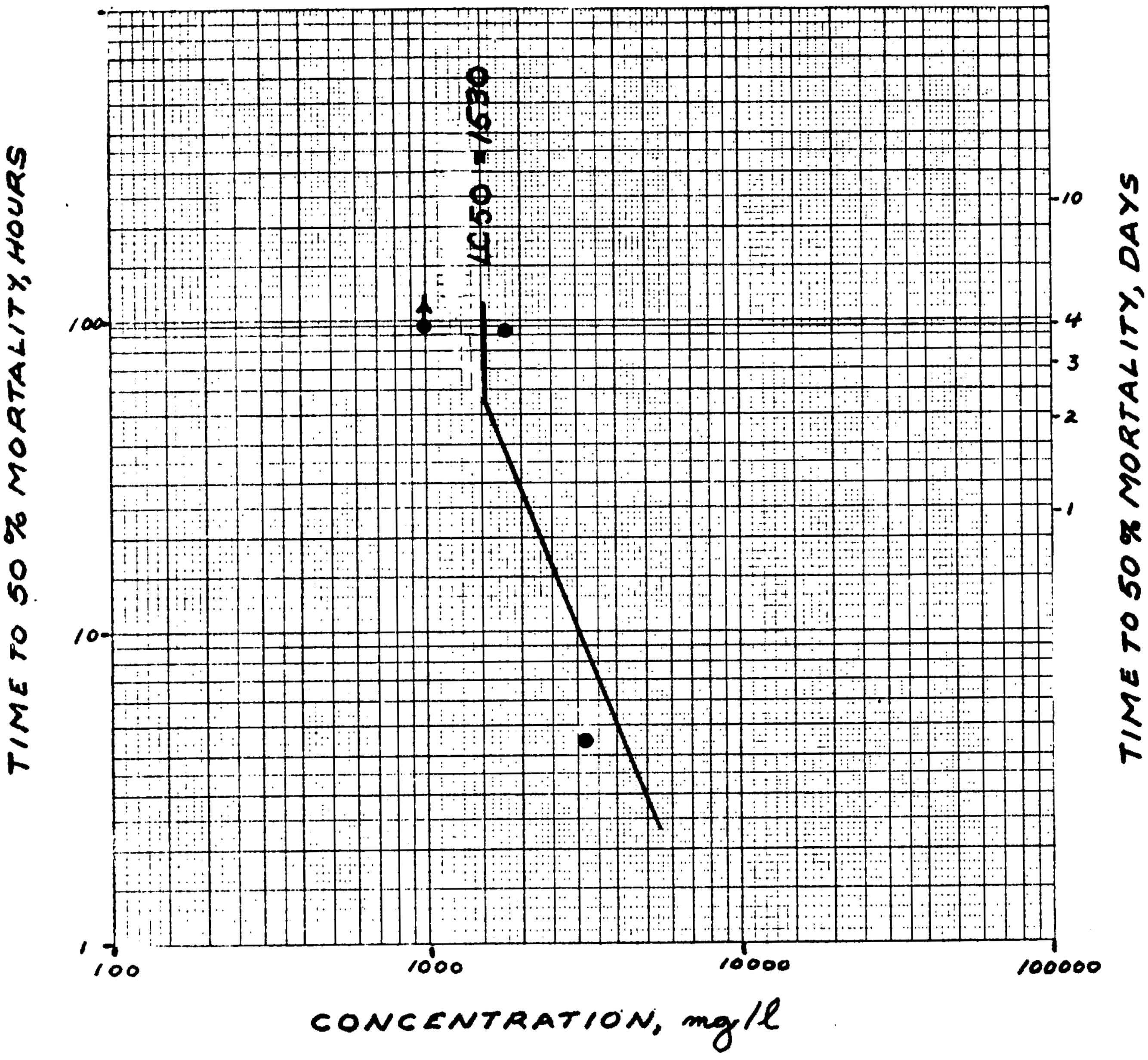

Fig. 9. Toxicity curve for Ferrochrome lignosulfonate tested against rainbow trout. This material is also known by the trade names Peltex and Q-Broxin.

The 96-hour LC50 was 1530 mg/ℓ. The 95% confidence limits were 1140 and 2050 mg/ℓ. The slope of the probit line was 8.439. The lethal threshold concentration was 1530 mg/ℓ. The toxicity curve (Fig. 9) is a simple one because only concentrations near the threshold were tested. Tests at higher concentration would have established better the right hand side of the curve. The lethal threshold concentration is almost certainly the same as the 96-hour LC50, since no fish died at 1000 mg/ℓ, during the following 10-day period when they were inadvertently left in solution.

All of the chemical dissolved in the test water, colouring the water a dark brown. There was a decrease in pH at higher concentrations. Prior to introduction of chemical, pH of the water was 8.5. After the introduction, pH dropped and then remained constant at pH 7.7, 7.5, 7.2, and 6.7, going from weak to strong concentration.

Sodium Acid Pyrophosphate (S.A.P.P.) ($Na_4P_2O_7 \cdot 10H_2O$)

This chemical is also known as tetrasodium pyrophosphate decahydrate (Merck). It is a dispersant for treating cement contamination, and it can be used as a rust inhibitor and remover (Merck Index).

The 96-hour LC50 was 870 mg/ℓ. The 95% confidence limits were 662 and 1140 mg/ℓ, and the slope of the probit line was 10.27. Concentrations near the threshold were tested resulting in a simple toxicity curve. The lethal threshold concentration was probably the same as the 96-hour LC50 since all mortality took place within the first 31 hours (Fig. 10).

The pH was 8.5 before the introduction of the chemical. After the introduction of S.A.P.P. the pH dropped and then remained constant at the new levels for the remainder of the test period. The pH values in the test tanks were 6.5, 6.25, 6.0, and 5.5, going from weak to strong concentrations. The pH values of 6.0 and above would not be acutely toxic to fish, so the LC50 would represent the toxicity of the S.A.P.P., not of pH. Water hardness followed a corresponding pattern. The hardness values expressed as $CaCO_3$ were 220, 65, 35 and 0, again going from weak to strong concentrations. It looks like S.A.P.P. was acting as a chelating agent for the calcium and magnesium ions in the water.

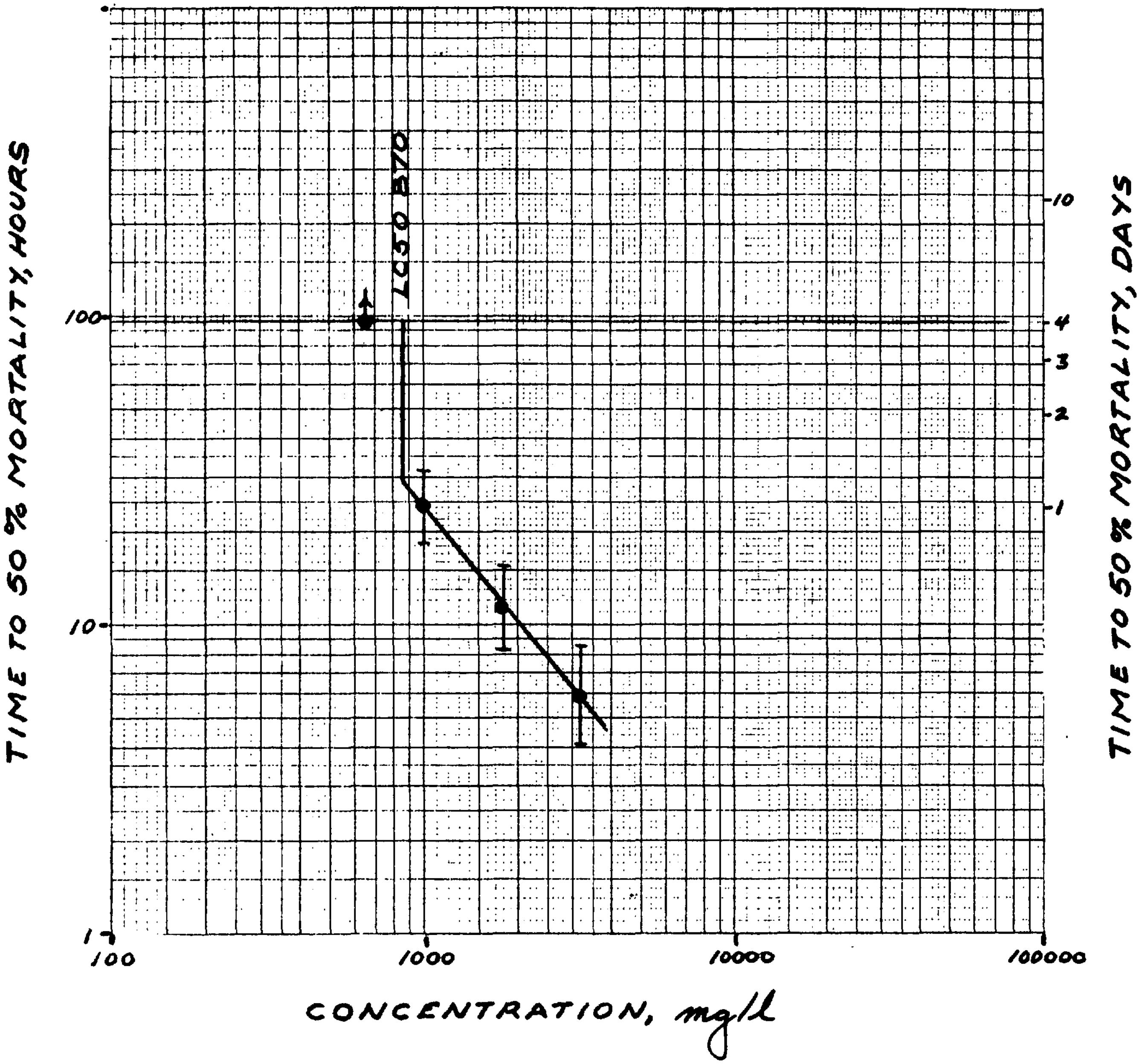

Fig. 10. Toxicity curve for sodium acid pyrophosphate tested against rainbow trout.

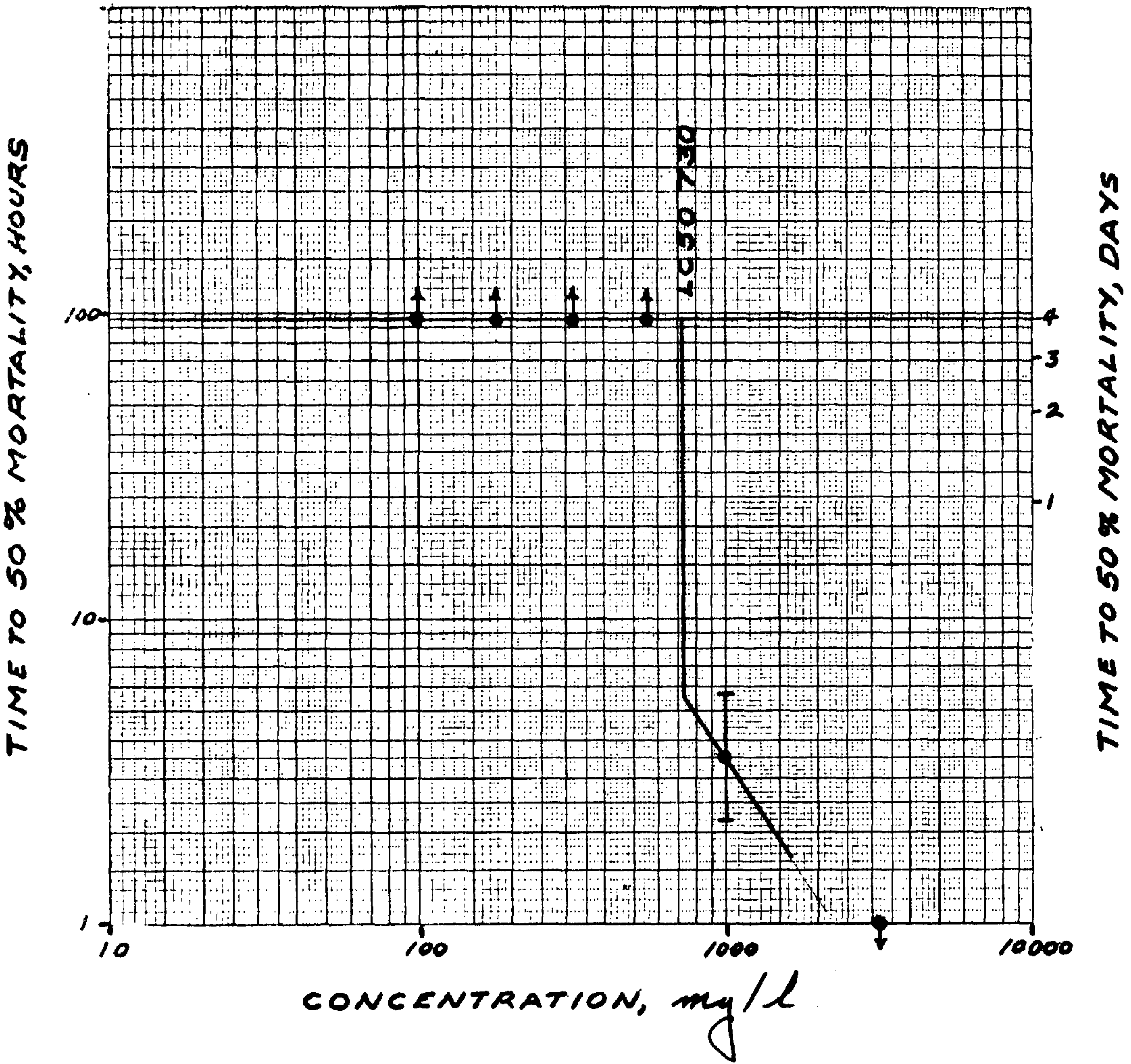

Fig. 11. Toxicity curve for Potassium Chrome Alum (Chromalit) tested against rainbow trout.

Potassium Chrome Alum (Chromalit)

This chemical is an alum and is known generically as potassium chromium sulfate ($K\,Cr\,(SO_4)_2.12H_2O$). Its function is not known to us.

The 96-hour LC50 was between the limits of 560 and 1000 mg/ℓ. An informal estimate of the LC50 would be 730 mg/ℓ. Only the concentrations near the threshold were tested resulting in an apparently simple toxicity curve (Fig. 11). To establish the right-hand side of the curve 3200 mg/ℓ was tested, but death was instantaneous, almost certainly because of pH below 5.5. The lethal threshold concentration was the same as the 96-hour LC50 since all mortality took place within the first six hours. This is probably a result of the toxicity being caused by low pH. All of the chemical dissolved initially, colouring the test water a blue-grey, then a precipitate formed on the tank bottom. Immediately after the introduction of the chemical, pH dropped, then rose within 24 hours and remained constant for the remainder of the test. The initial pH values in the test tanks, going from weak to strong, were 7.5, 7.0, 6.5, 6.0 and 5.5. The lowest pH may have been the primary cause of toxicity, but values of 6.0 and greater would not cause acute mortality. After 24 hours the pH stabilized at 7.7 to 7.5. Water hardness followed the same trend with initial readings from weak to strong of 325, 310, 285, 270 and 250 all expressed as $CaCO_3$. At 24 hours, hardness had returned in all tanks to 330-320 mg/ℓ. Chemical reactions within the water are unknown.

Ben-Ex

Ben-Ex is a copolymer of polyvinyl acetate and maleic anhydride (ratio not published). It is used primarily as a viscosifier, and as an extender for bentonite.

The 96-hour LC50 was 664 mg/ℓ. The 95% confidence limits were 527 and 836 mg/ℓ. The slope of the probit line was 11.4. As mortality continued up to the 89th hour it is suspected that the lethal threshold concentration would be lower than the 96-hour LC50. A simple toxicity curve was evident (Fig. 12).

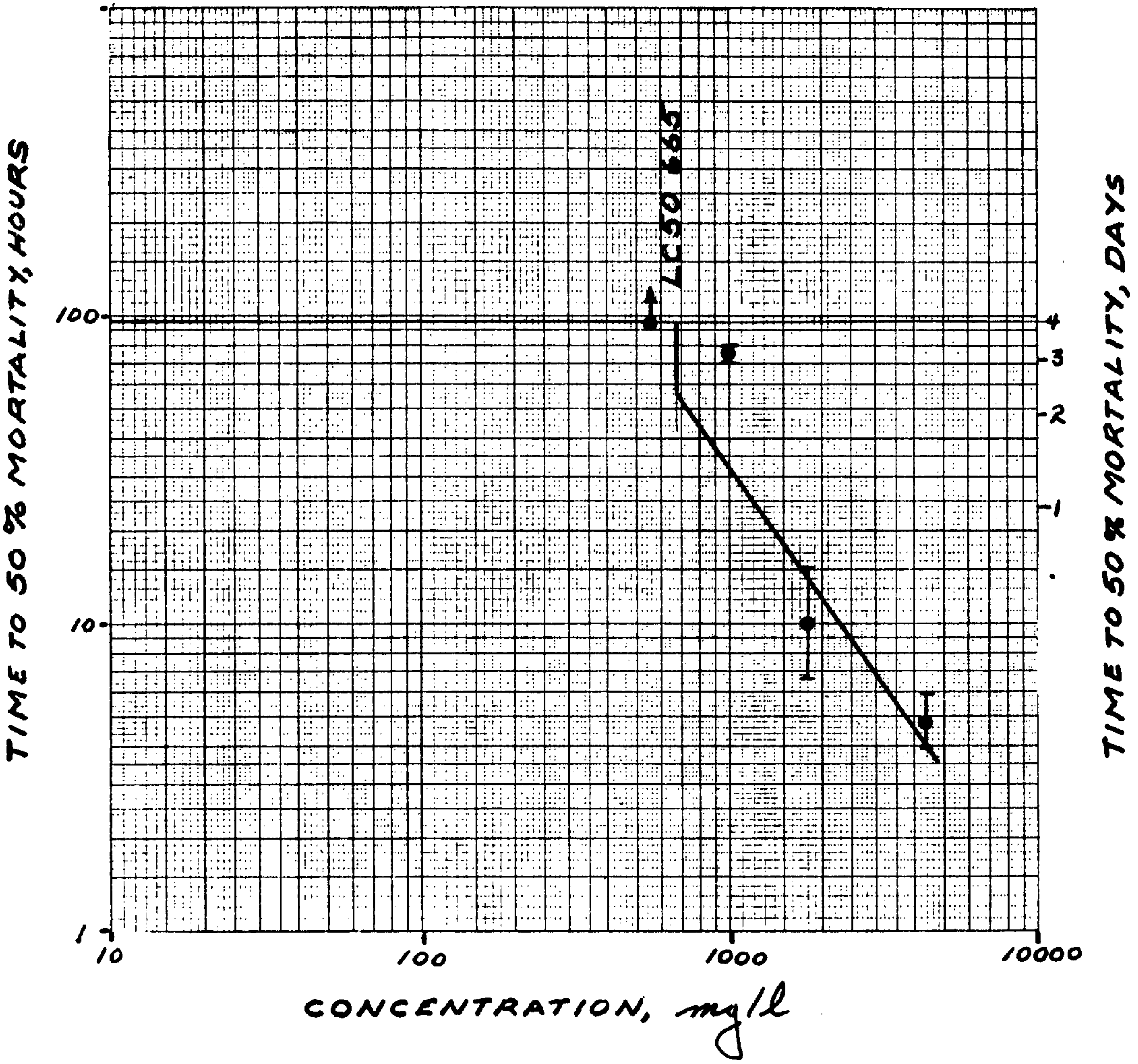

Fig. 12. Toxicity curve for Ben-Ex tested against rainbow trout.

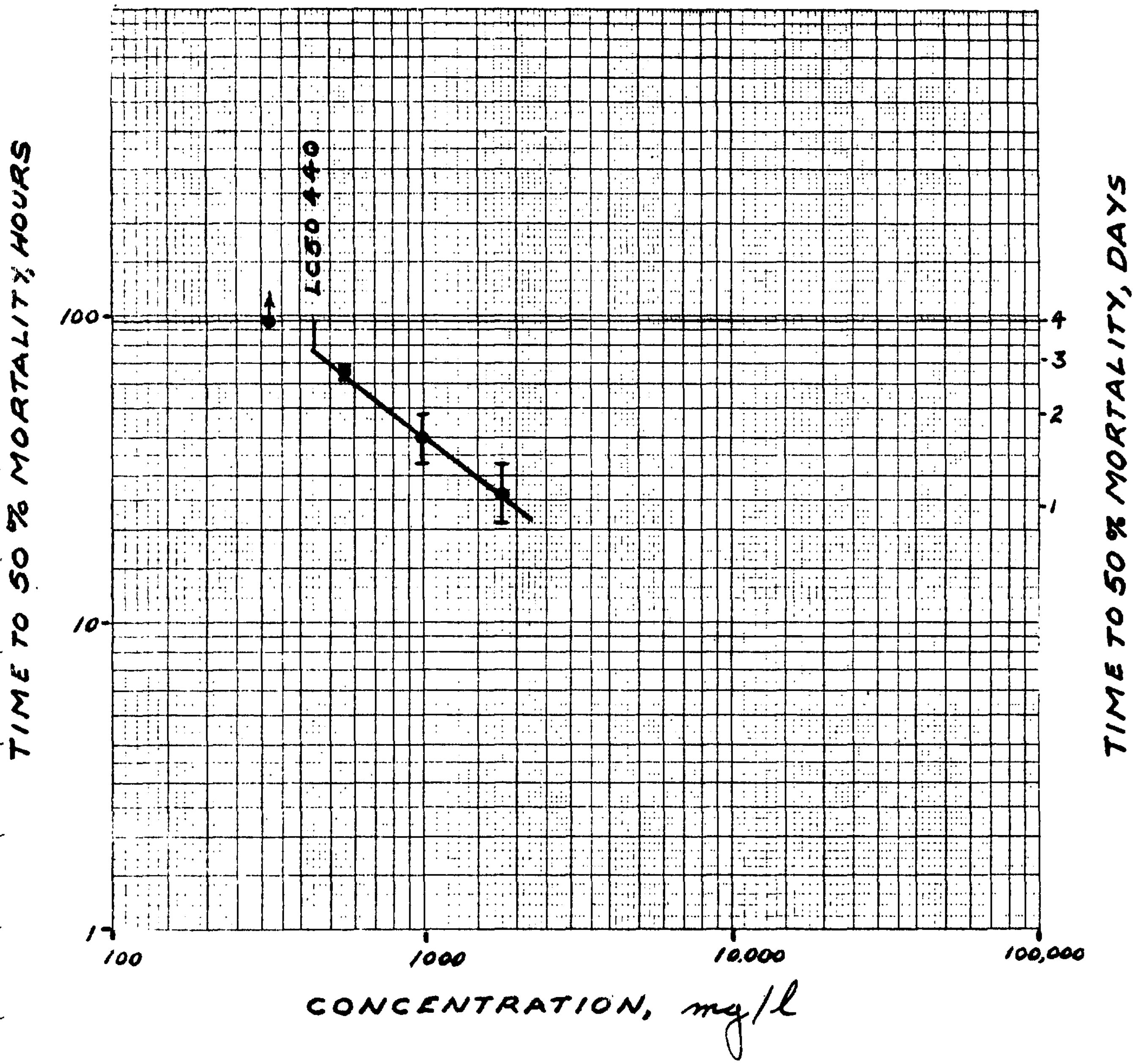

Fig. 13. Toxicity curve for Kelzan-XC tested against rainbow trout.

The chemical was blended with the test water prior to its introduction into the test tank. This created a light pink viscous layer which slowly sank to the bottom of the tank. After 12 hours the colour disappeared. For the first few hours of the test, the test solution gave off a strawberry-like odour.

Kelzan-XC

This is an industrial grade Xanthan gum. It is a viscosifier and fluid loss control additive.

The 96-hour LC50 was between the limits of 320 and 560 mg/ℓ. An informal estimate of the LC50 would be 440 mg/ℓ. The lethal threshold concentration was probably the same as the 96-hour LC50 since all mortality took place within 68 hours (Fig. 13).

Prior to its introduction into the test tanks the chemical was blended with test water. In the test tanks, the chemical floated on the surface giving the appearance of floating balls of cotton wool.

Metso Beads

This chemical is used for corrosion control. Its chemical composition is unknown, but it was soluble.

Tests were not quite completed, because a rather small sample of material was received. The LC50 and toxicity curve were not established with certainty. However, the 96-hour LC50 would be between 100 and 560 mg/ℓ, probably in the vicinity of 300 mg/ℓ.

Caustic (Celanese)

This chemical was received as a flake. Its generic name is sodium hydroxide (NaOH). It is used primarily as an acidity control additive and secondarily as a bactericide or as a calcium remover.

The 96-hour LC50 was 105 mg/ℓ. The 95% confidence limits were 81 and 136 mg/ℓ. The slope of the probit line was 6.34. The lethal threshold concentration is the same as the 96-hour LC50 since all mortality took place within the first 40 hours (Fig. 14).

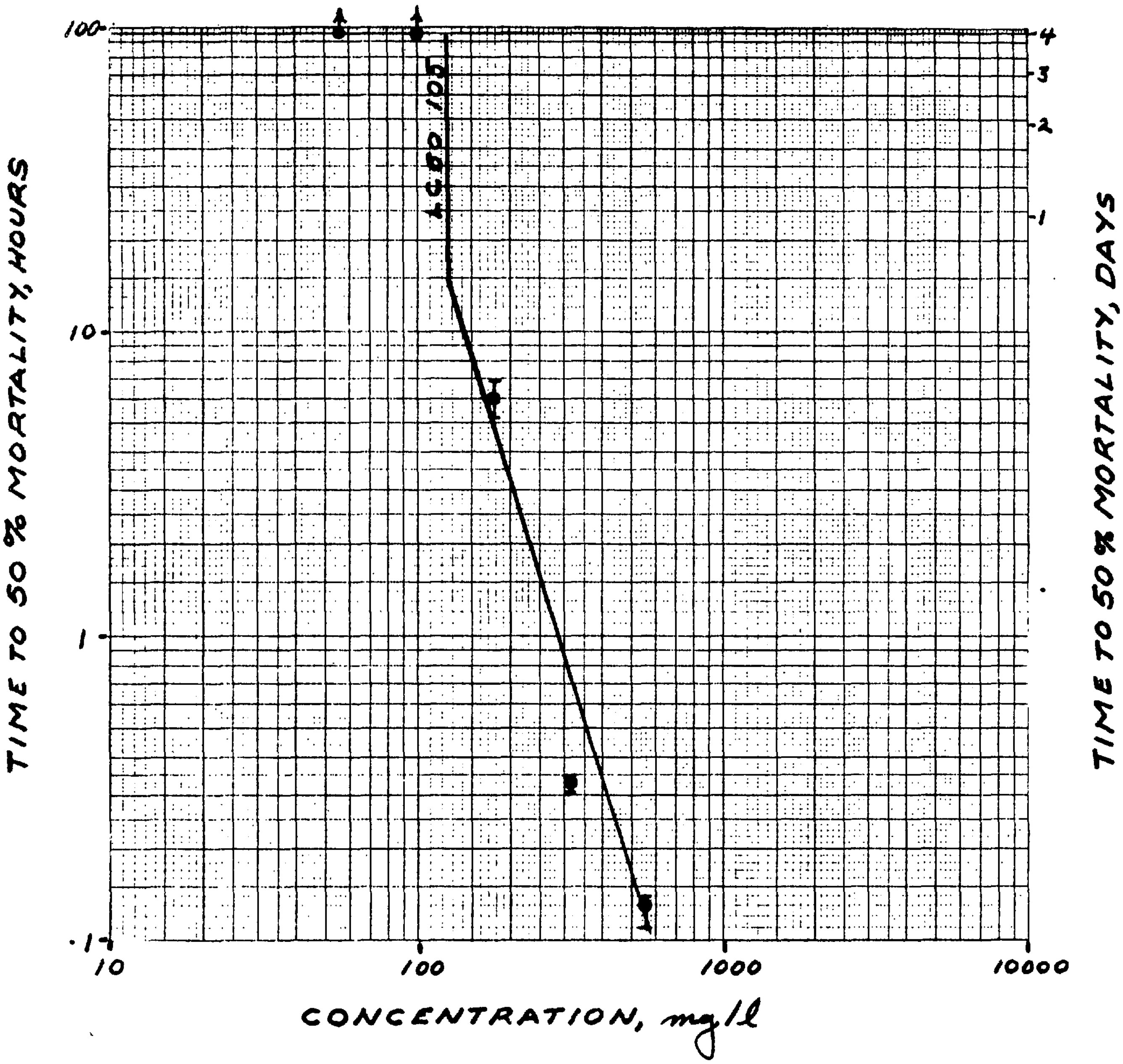

Fig. 14. Toxicity curve for Caustic (Sodium hydroxide), tested against rainbow trout.

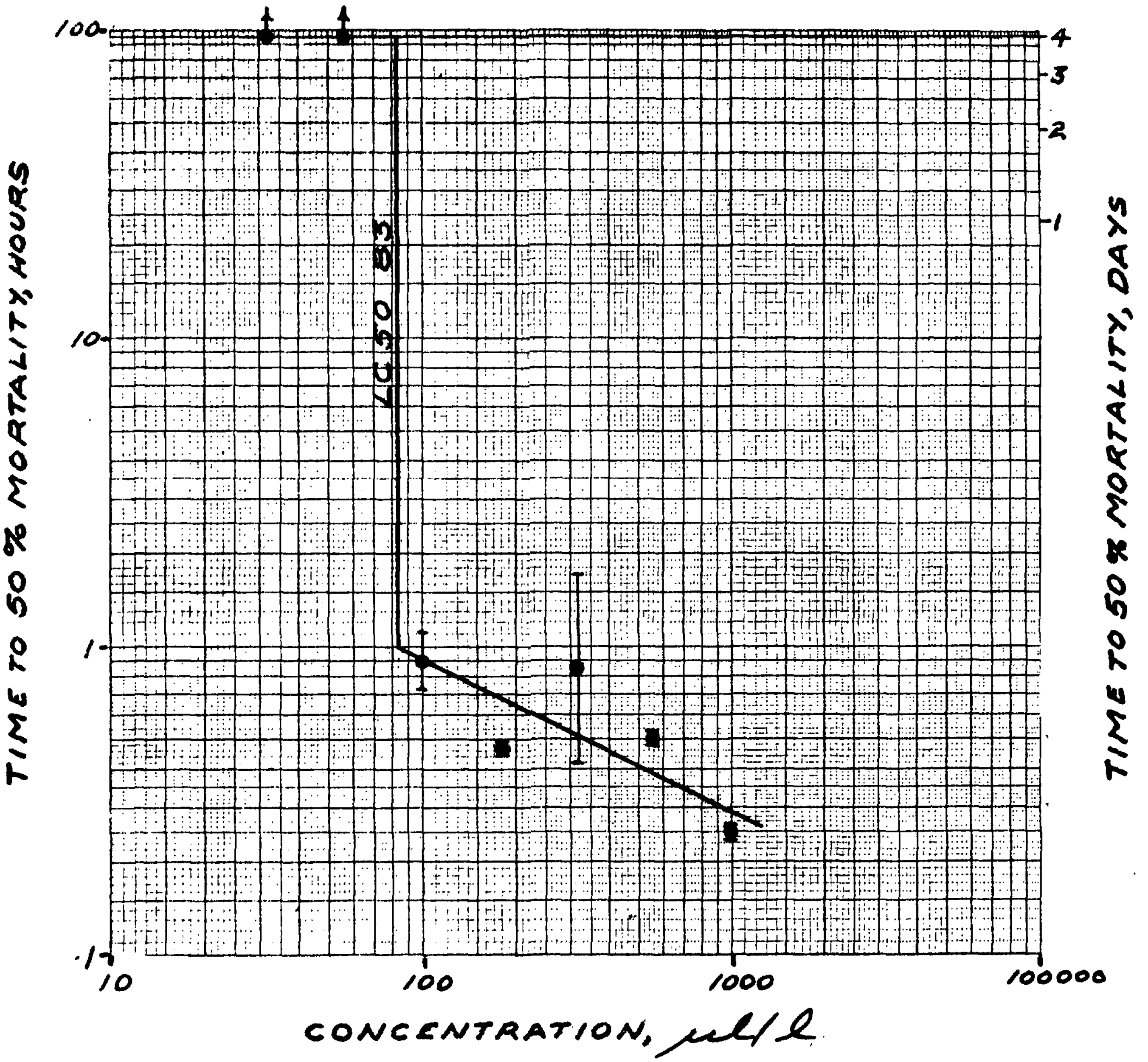

Fig. 15. Toxicity curve for Capryl Alcohol tested against rainbow trout.

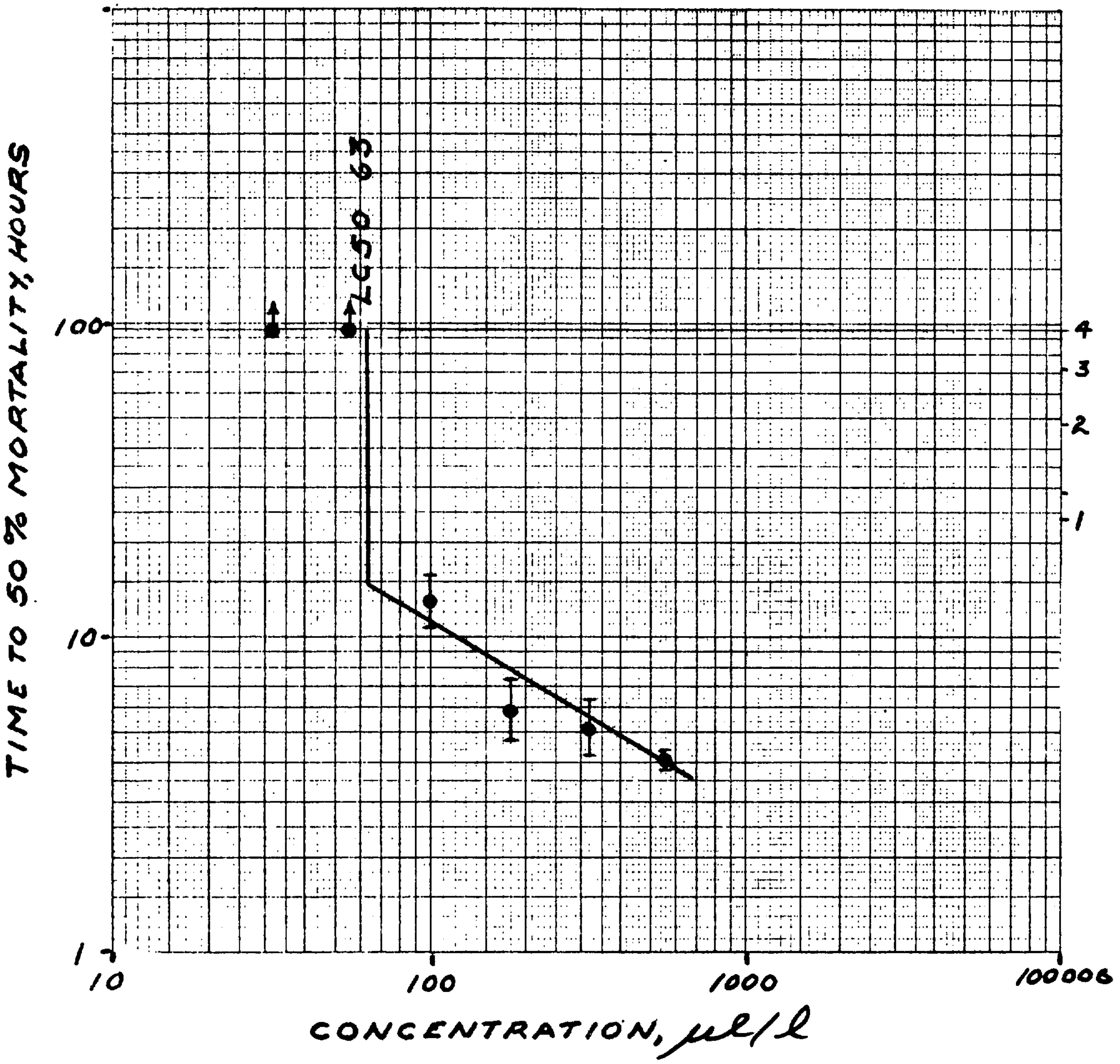

Fig. 16. Toxicity curve for Tricron tested against rainbow trout.

All of the chemical dissolved initially but then an off-white coloured precipitate formed on the tank bottom, no doubt calcium carbonate. Water hardness was decreased to 340, 300, 220, 190, 170, 120, and 50 mg/ℓ, going from weak to strong concentrations. The pH was raised as would be expected, to levels of 8.5, 9.0, 10.0, and greater than 10, again going from weak to strong concentrations.

Fish died at concentrations causing pH above 10 which is exactly what would be expected from the literature.

Capryl Alcohol

This material was completely soluble. We do not know its function.

The 96-hour LC50 was between the limits of 56 and 100 μℓ/ℓ. An informal estimate of the LC50 would be 83 μℓ ℓ. The toxicity curve was straightforward (Fig. 15). Mortality was very rapid, and none occurred after an hour. The threshold LC50 is therefore the same as the 96-hour LC50.

Tricron

Tricron is a surface wetting agent composed of 30% dihydroxypropane, 2% inorganic salts, 15% surfactant blend (mixture of tall oil soaps and alkyl aryl sulfonates) and 53% water. All of this material dissolved in water.

The 96-hour LC50 was 63μℓ/ℓ, with confidence limits of 46 and 87μℓ/ℓ. The slope of the probit lines was 5.87. The toxicity curve (Fig. 16) was a simple one, with all mortality occurring within the first 17 hours. The threshold LC50 is accordingly the same as the one given above.

Paraformaldehyde

Paraformaldehyde (CH_2O) was received as a powder. It had been formed from a concentrated formaldehyde solution. It is used as a bactericide.

The 96-hour LC50 was 60 mg/ℓ. The 95% confidence limits were 46 and 78 mg/ℓ, and the slope of the probit line was 6.02. The right-hand side of the toxicity curve was straight and well documented (Fig. 17). Since 40%

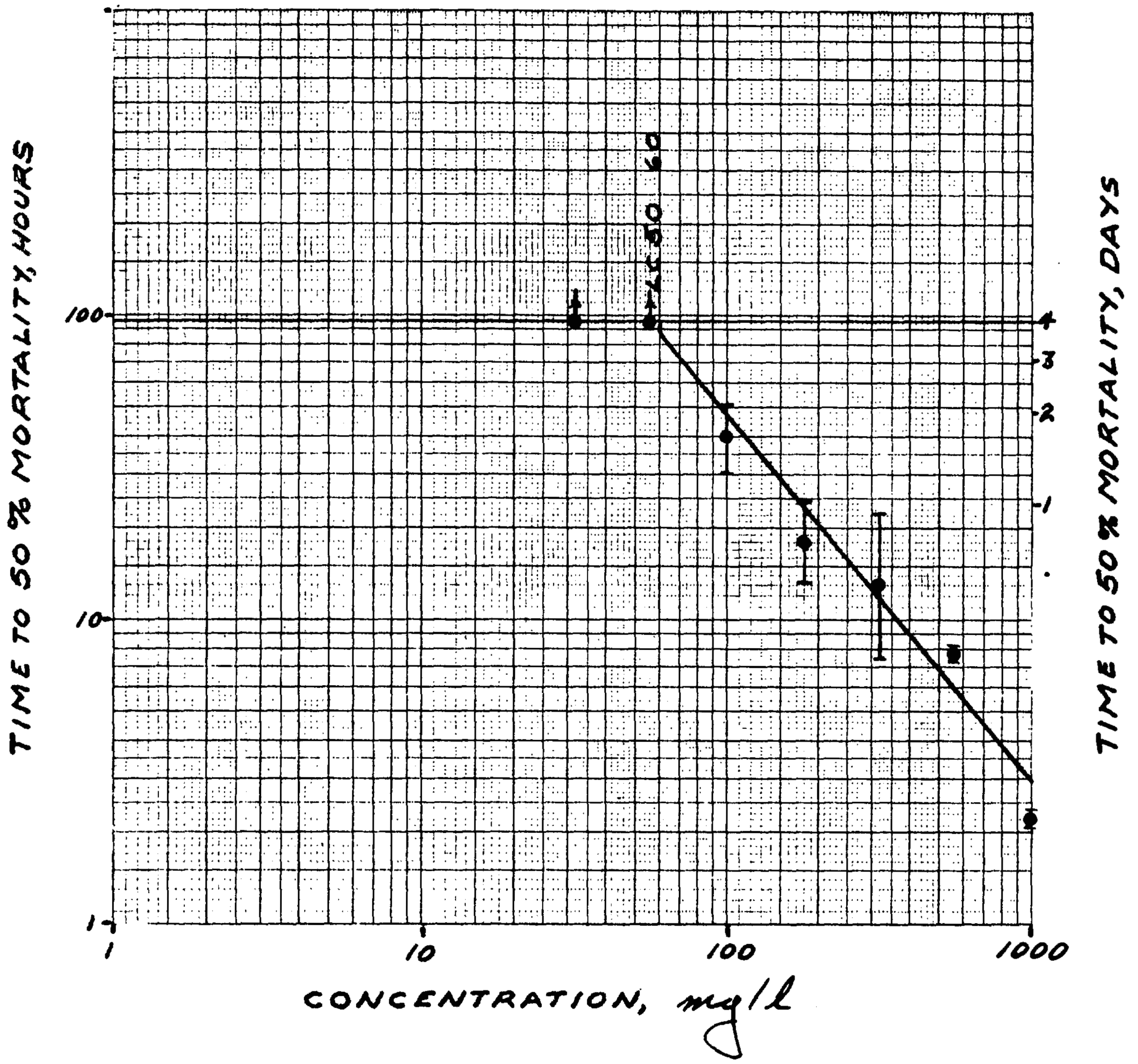

Fig. 17. Toxicity curve for paraformaldehyde tested against rainbow trout.

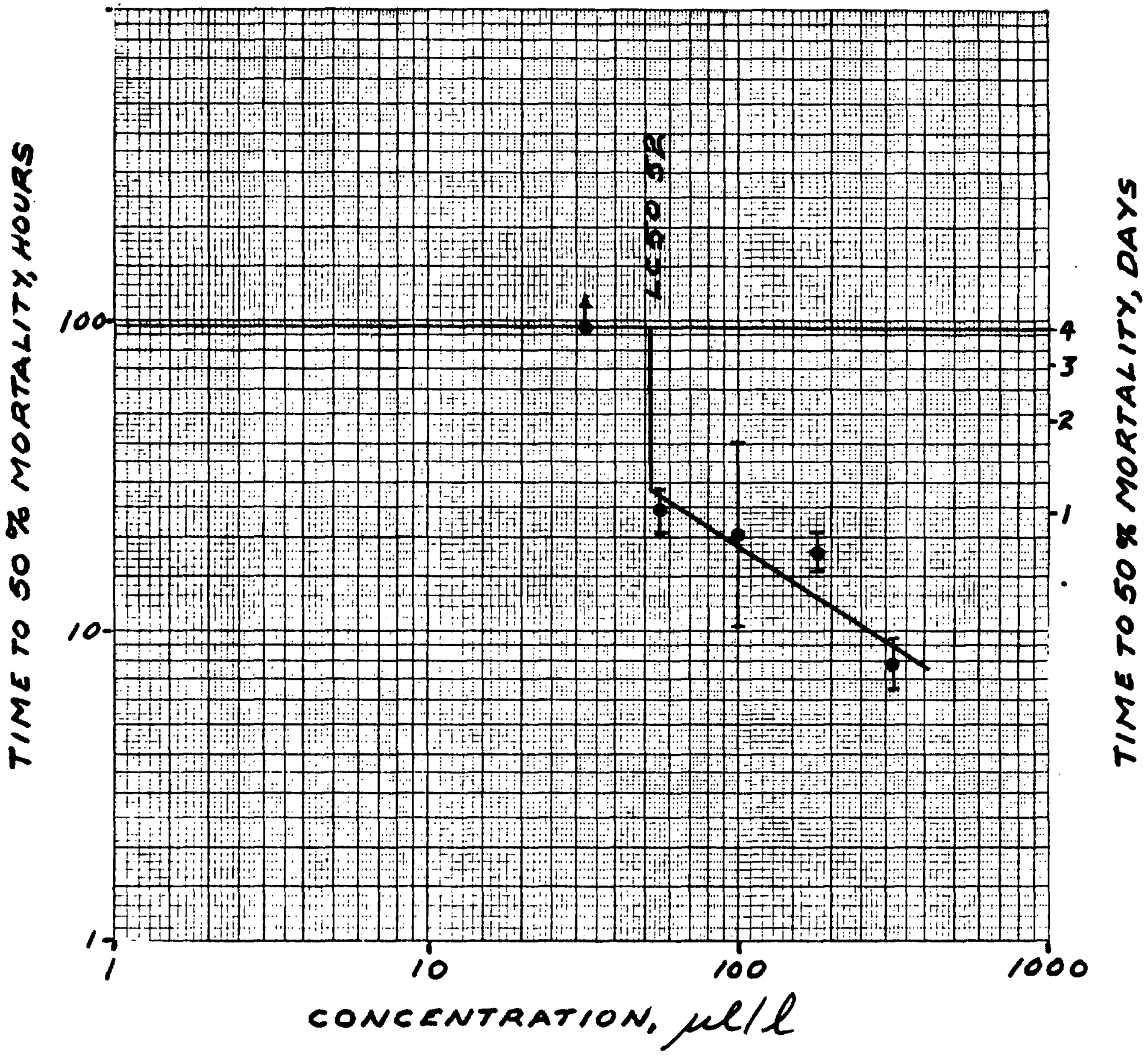

Fig. 18. Toxicity curve for Skot-Free tested against rainbow trout.

mortality of the test fish occurred at 85 hours in the 56 mg/ℓ test solution, it is suspected that the threshold lethal concentration would be somewhat lower than the 96-hour LC50 given above.

Skot-Free

Skot-Free is a surface active agent composed of latent liquid solvent, mixed alcohols, and still bottoms of indeterminate chemical composition. It is used as a surface active agent. All of this material was soluble in water.

The 96-hour LC50 was 52μℓ/ℓ. The 95% confidence limits were 36 and 76μℓ/ℓ, and the slope of the probit line was 4.54. The toxicity curve is a simple one. The lethal threshold concentration is the same as the 96-hour LC50 since all mortality took place within the first 25 hours (Fig. 18).

Swift's Rig Wash

This was obtained as a granular material. Its composition is unknown, but it dissolved in water. It is presumably a surface active agent, for washing equipment.

The 96-hour LC50 was 22 mg/ℓ. The 95% confidence limits were 11 and 42 mg/ℓ, and the slope of the probit line was 3.31. As mortality continued up to 96 hours the lethal threshold concentration may not have been established, but the toxicity curve is a simple one (Fig. 19).

B-Free

B-Free, a surface active agent of unknown composition, was completely soluble in water.

The 96-hour LC50 was 19.2μℓ/ℓ. The 95% confidence limits are 14.8 and 24.9μℓ/ℓ. The slope of the probit line is 6.18.

B-Free is relatively slow in causing mortality (Fig. 20). A concentration three times the LC50 did not result in 50% mortality until 60 hours of exposure. Since mortality was continuing at 96 hours, tests were run for 10 days. The threshold LC50 was between the limits of 5.6 and 10 μℓ/ℓ. An informal estimate of the LC50 would be 7.5 μℓ/ℓ. Aside from the long exposure times, the toxicity curve was normal.

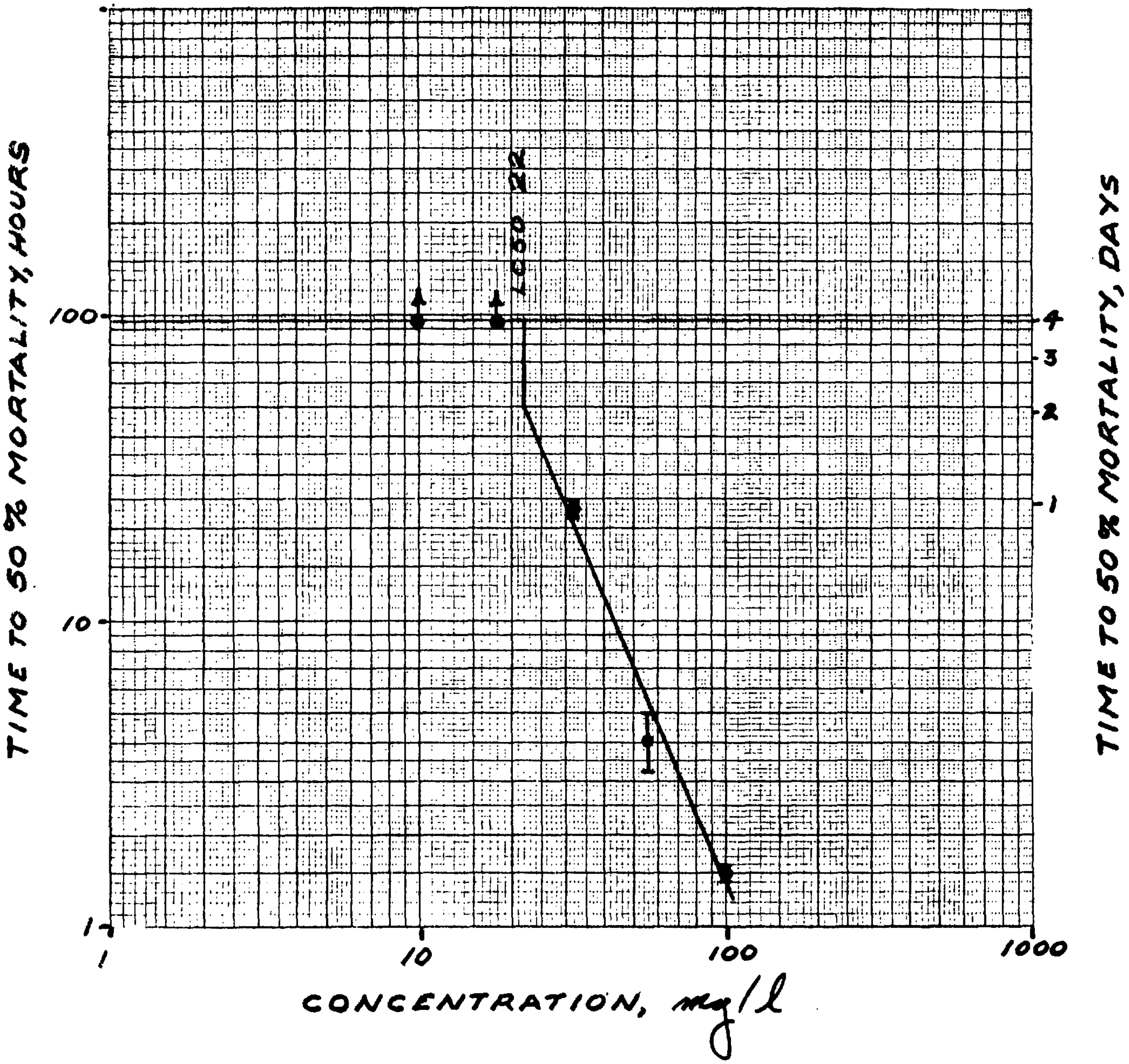

Fig. 19. Toxicity curve for Swift's Rig Wash tested against rainbow trout.

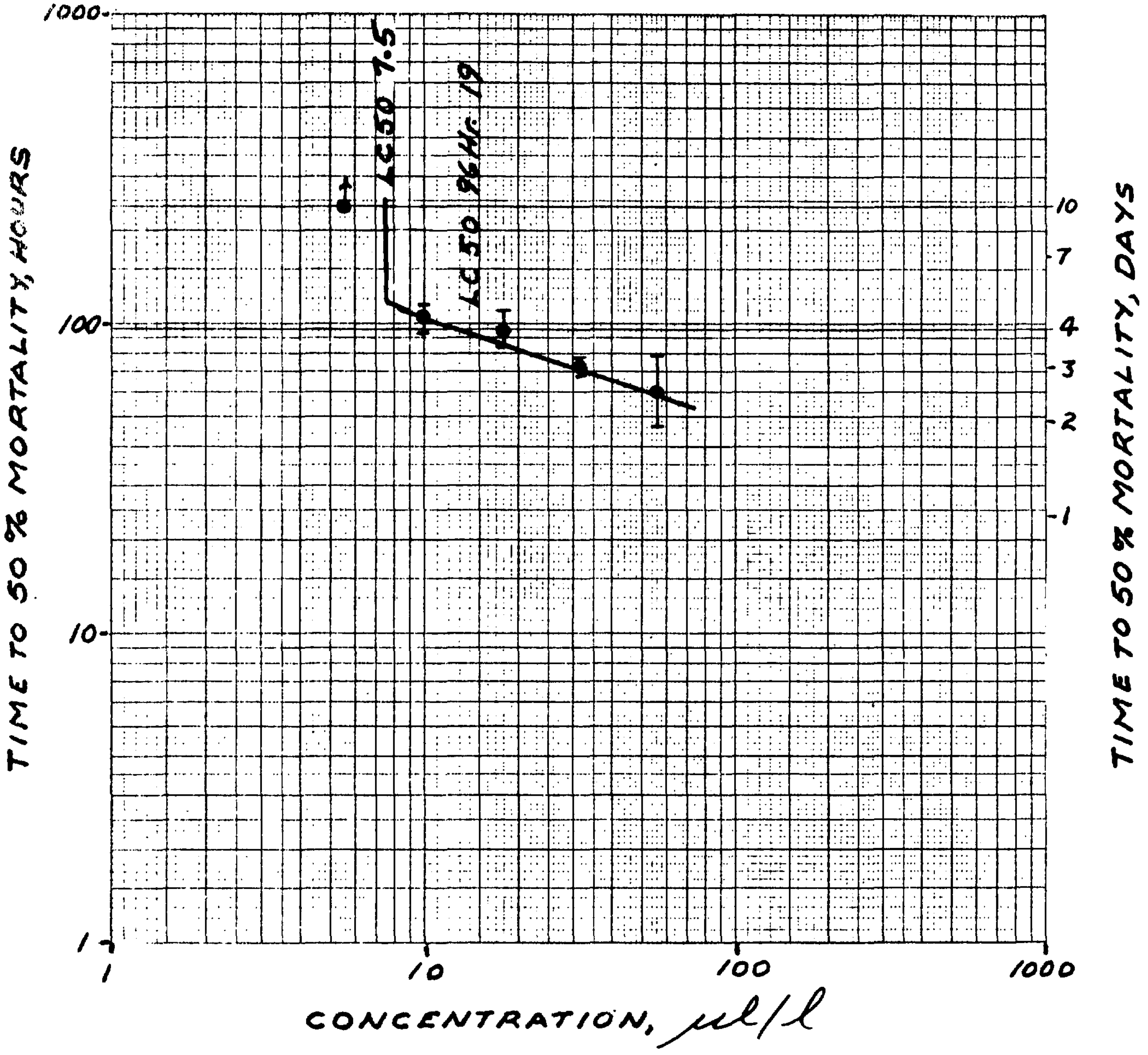

Fig. 20. Toxicity curve for B-Free tested against rainbow trout. The lower LC50 is a ten-day value and is the threshold LC50.

Dominion Rig Wash

This was obtained as a granular material of unknown composition. It dissolved in water. It is no doubt a surface active agent used for washing equipment.

The 96-hour LC50 was between the limits of 10 and 18 mg/ℓ. An informal estimate of the LC50 would be 14 mg/ℓ. As mortality continued up to the 84th hour it is suspected that the lethal threshold concentration was not determined. The toxicity curve (Fig. 21) is a straightforward one.

FLR-100, Staflo, and SS-100

The first two of these chemicals are fluid loss reducers, and the third is a shale stabilizer. We do not know their chemical compositions.

From the preliminary results, it may be stated that all three materials failed to cause mortality at 1000 mg/ℓ. It was not possible to establish toxicity curves, nor LC50's, because of the small amounts of material supplied.

Prior to their introduction into the test tanks, the chemicals were blended with test water. After being introduced, they each formed a transparent viscous layer on the tank bottom.

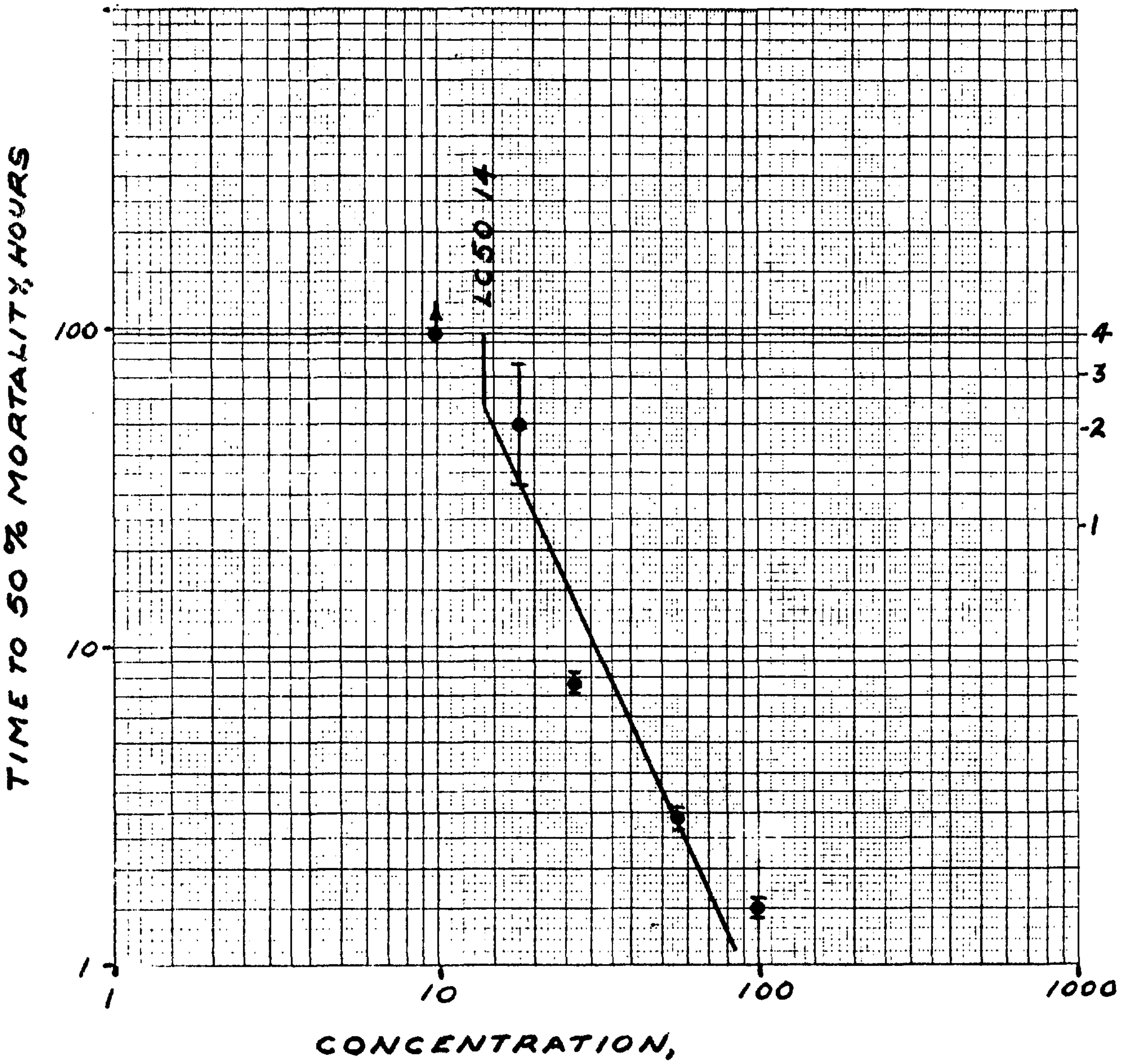

Fig. 21. Toxicity curve for Dominion Rig Wash tested against rainbow trout.

DISCUSSION

About half of the components of drilling fluids which were evaluated (13 out of 27) were lethal at concentrations below 1000 p.p.m., and the remainder at higher concentrations. Of the more toxic half, the majority were surfactants of one kind or another, or obvious poisons such as paraformaldehyde. It seems pointless in this day and age to use poisonous chemicals in situations where they might eventually contaminate the environment. Their use should be discontinued and non-toxic materials substituted as necessary. This approach seems feasible. For example, oil dispersant manufacturers came up with less toxic dispersants, rather soon after the damage done by toxic ones at the time of the Torrey Canyon oil spill.

Kelzan-XC had an LC50 of 440 mg/ℓ. However, the material called Kelzan XC Polymer Al is more toxic by an order of magnitude, according to preliminary tests by the Alberta Energy Resources Conservation Board (D.R. Shaw, indirect personal communication).

It is interesting that general opinion within the drilling industry is that Kelzan-XC (and sister materials under other trade names) should be perfectly safe as far as toxicity is concerned. It is a bacterial product of sugar beets, a complex organic polymer. The food grade of this xanthan gum is considered perfectly safe and is used in foods such as salad dressing. Yet it is obvious that the material kills at fairly low levels. Such an example shows that there is some benefit in actually testing these potential pollutants, rather than assuming too much from previous "general knowledge".

In some of the surfactants, (Swift's Rig Wash, B-Free, and Dominion Rig Wash) mortality continued beyond 96 hours, or almost up to that time. B-Free was tested for 10 days, at which time the LC50 was lowered to half of the 96-hour value. Possibly the other two might have had similarly lower values for longer tests.

The use of pumps to agitate the testwater was partially successful in keeping solids suspended. The rationale may not immediately be apparent to those thinking about what happens in the field. However, the objective is the same as in most other laboratory bioassays--to expose groups of test-organisms to a series of constant levels of the stressing-factor. From the reactions to the constant levels, one may predict the reactions in a field situation in which the levels may be changing all the time. In this case, a spill of drilling fluid into natural waters would result in high concentrations of suspended solids at first, then lower and lower concentrations as the solids settled out. There is reasonable hope of predicting the effects of such a changing situation, on the basis of time-concentration summations from laboratory work at constant concentrations. However the opposite approach is not very profitable--it is almost impossible to analyse experiments with continually changing parameters, let alone predict from such experiments to a real situation.

Theoretical toxicity of drilling fluids compared with actual toxicity.

It seems worthwhile to make a comparison between the theoretical and actual toxicity of drilling fluids, however rough and approximate the exercise may be. Tables I and II list the total components used in the drilling fluids tested, Imperial Oil's Rig 51 and Gulf's Rig 15. These totals have been put together from logs of these rigs. They are listed in order from most toxic to least toxic.

The second column gives the number of pounds of the material used, during the drilling operation. It is assumed that the drilling fluid is half water by weight, an assumption that is probably reasonably close to the truth.

The third column results from a simple calculation to express each component as a concentration, in parts per million by weight, in the total fluid.

The fourth column states the LC50 of each component as given in the Results section of this report. It has been necessary to neglect the components at the bottom, for which we do not know the LC50's, but these seem relatively unimportant.

Table I. List of components used in drilling fluid system of Imperial Oil Limited Rig 51, from April 30 to June 30 and July 20 to August 17, 1972*

	No. of lbs. used	Parts per million in whole fluid**	LC50, p.p.m.	Toxic units
Caustic soda	12,000	4,420	105	42
Kelzan	3,800	1,400	440	3.2
Chrome alum	960	354	732	0.48
Ferrochrome lignosulfonate	11,890	4,380	1,530	2.9
Potash (KCl?)	58,000	21,400	2,020	11
Sodium bicarbonate	800	295	7,550	.04
Barite	861,850	318,000	>7,500	<42
Bentonite	204,400	75,300	>10,000	<7.5
<u>Toxicity Not Known</u>				
Plaster	3,050	1,120	-	-
Oil well cement	3,000	1,100	-	-
Permafrost cement	198,000	73,000	-	-
Sub-totals	1,356,886	501,000		
Water	1,356,886	500,000		0
Totals	2,713,772	1,000,000**		<109

*data for about 3 weeks in July not available at time of writing.

**does not add exactly because of rounding to three significant figures.

The fifth column merely expresses the toxic contribution of each component in the fluid, according to the fraction

$$\frac{\text{actual concentration in the fluid, p.p.m.}}{\text{lethal concentration, p.p.m.}}$$

This measuring-unit of toxic concentration has been called the "toxic unit" (Sprague, 1969). On this scale, 1.0 toxic units will just kill fish, while anything less than 1.0 toxic units will not.

Adding up toxic units, we have a total of <109 toxic units for drilling fluid from Imperial Oil Rig 51. Neglecting the "less than", which is admittedly a large omission, we may now make a prediction of the toxicity of the fluid. The total toxic units is actually the numerical value of the dilution required to arrive at exactly the threshold LC50. Thus the LC50 = $\frac{1}{109}$ = 0.0092, or expressed as a percentage = 0.92%. This is reasonably close to the value of 0.83% which was obtained on the first estimate of LC50 from Rig 51.

It will be noted that almost half of the toxic units (42) come from the caustic soda. If this were neutralized, as would often be the case, and was the case in the second sample from Rig. 51, it would lose its toxicity which is almost all because of pH. Therefore if we assume neutralization, total theoretical toxic units become 109 -42 = 67. Accordingly, the LC50 would be estimated as $\frac{1.0}{67}$ = 0.015 or 1.5%. This is getting closer to the value of 5.3% obtained for the LC50 of the second sample of waste from Rig 51, which was more nearly neutral. Although there is a factor of 3.5 x between the predicted and measured LC50's, this cannot be considered very large considering all the generalizations which were made.

Turning to results from Rig 15 (Table II), the total toxic units is <1.02. Again neglecting the "less than", the theoretical LC50 of this waste may be estimated. However, this waste was not alkaline when it was received. In other words, the toxicity of the caustic soda should be discounted, since it was apparently neutralized. The total toxic units would then be 102 -51 = 51. The lethal concentration would be predicted as $\frac{1.0}{51}$ = 0.0196 or 1.96% or about 2% fluid.

Table II. List of components used in drilling fluid system of Gulf Rig 15, from May to August 8, 1972, and approximate calculations of theoretical toxicity to fish.

	No. of lbs. used	Parts per million in whole fluid	LC50	Toxic units
Caustic soda	13,000	5,330	105	51
(Kelzan) XC	8,795	3,600	440	8.1
Benex	99	40.6	665	.06
Ferrochrome lignosulfonate	6,150	2,520	1,530	1.6
Potassium chloride	53,100	21,800	2,020	11.
Sodium bicarbonate	200	82.0	7,550	.01
Barite	371,700	152,000	>7,500	<20
Calcium chloride	4,800	1,970	>10,500	<.19
CMC	1,025	420	>10,000	<.04
Bentonite	234,800	96,200	>10,000	<9.6
Unical	4,855	1,990	-	-
Super Coll	73,650	30,200	-	-
Cement	448,000	184,000	-	-
Sub-totals	1,220,174	500,000		
Water	1,220,174	500,000		
Totals	2,440,348	1,000,000		<102

Again, this is not too different from the actual value of about 4.2% obtained on a grab sample of this fluid. It is different by a factor of only 2.1 x, which again must be regarded as rather close, all things considered.

It would seem reasonable to adopt as a working hypothesis, that the toxicities of the individual components are additive in drilling fluids. In other words, the overall toxicity of a drilling fluid can be predicted by adding up the toxicities of the individual components.

As a further observation on Tables I and II, it is interesting that two components make up most of the toxicity. Caustic soda is one which has already been discussed. It makes up $\frac{42}{<108}$ and $\frac{51}{<102}$ = approximately 39% and 50% of the total toxicity, if not neutralized. The other major contributor seems to be barite, with $\frac{42}{<108}$ and $\frac{20}{<102}$ = 39% and 20% of the total toxicity. Of course the contribution could be much more than those values. Barite is a major component of drilling fluids, 30% and 64% of total material used in these fluids.

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Appendix A

Test Results for Individual Concentrations of each Drilling Fluid and Constituent Chemical

	Concentration, % by volume	ET50 hours	95% confidence limits	% mortality at exposure of: 96 hr	specified hours	"S" = slope factor of Litchfield
	32.2	1.0	.91,1.1	100%	-	1.116
	10.1	1.3	.86,2.0	100%	-	1.105
	3.23	4.1	2.7,6.3	100%	-	1.544
Imperial	3.23*	5.3	3.6,7.8	100%	-	1.604
Rig 51 (July)	3.23	4.8	3.2,7.2	(combined data of above 2 tests)		1.435
	1.15	7.0	5.1,9.6	100%	-	1.475
	1.01	12.	5.5,24.	75%	100% at 144 hr.	2.134
	1.01*	19.	13.,28.	100%	-	1.800
	1.01	17.	9.9,30	(combined data of above 2 tests)		1.971
	0.755	-	-	25%	25% at 192 hr.	-
	0.564	-	-	0%	0% at 192 hr.	-
	0.324	-	-	0%	25% at 192 hr.	-
	0.181	-	-	0%	0% at 192 hr.	-
	0.10	-	-	0%	0% at 192 hr.	-
	0 (Control)	-	-	0%	0% at 192 hr.	-
Imperial Rig 51 (September)	10.0	9.4	6.1,15	100%	-	1.721
	5.66	-	-	40%	40% at 120 hr.	-
	3.20	-	-	20%	20% at 120 hr.	-
	1.83	-	-	0%	0% at 120 hr.	-
	1.0	-	-	0%	0% at 120 hr.	-
Gulf Rig 15	10.0	8.8	5.8,13	100%	-	1.584
	5.60	14.2	9.1,22	100%	-	1.647
	3.20	-	-	0%	0% at 168 hr.	-

*Test was done using very hard dilution water (353 mg/ℓ) as used for tests with all other chemicals and drilling fluids. Other tests with this unlabelled sample used water of 120 mg/ℓ hardness.

Chemical	Concentration mg/ℓ	ET50 hours	95% confidence limits	% mortality 96 hrs.	"S"
Gypsum	Not Tested, See Results				
Bentonite	10,000	-	-	0%	-
CMC-Regular	10,000	-	-	0%	-
	1,000	-	-	0%	-
	100	-	-	0%	-
	10	-	-	0%	-
CMC-Hi Vis	10,000	-	-	0%	-
	1,000	-	-	0%	-
	100	-	-	0%	-
	10	-	-	0%	-
Calcium Chloride	Not Tested , See Results				
Aluminium Stearate	Not Tested, See Results				
Barite	Not Tested				
Sodium Bicarbonate	Not Tested, See Results				
Torq-Trim	10,000	22.6	18.5,27.6	100%	1.124
	5,600	30.1	27.0,34.8	100%	1.176
	3,200	69.0	59.8,79.6	60%	1.156
	1,800	-	-	40%	-
	1,000	-	-	0%	-
Potassium Chloride	Not Tested, See Results				
Ferrochrome Lignosulfonate	5,600	0	-	100%	1.00
	3,200	4.5	-	100%	1.00
	1,800	94.	92,96	80%	1.020
	1,000	-	-	0%	-

S.A.P.P.	5,600	-	-	100%	1.00
	3,200	5.9	4.06,8.55	100%	1.522
	1,800	11.4	8.39,15.5	100%	1.405
	1,000	24.5	18.3,31.8	80%	1.382
	560	-	-	0%	-
Chromalit	1,000	3.54	2.2,5.7	100%	1.75
	560	-	-	0%	-
	320	-	-	0%	-
	180	-	-	0%	-
	100	-	-	0%	-
Ben-Ex	3,200	4.8	3.95,5.85	100%	1.253
	1,800	10	6.6,15.0	100%	1.58
	1,000	76	72.6,79.6	100%	1.038
	560	-	-	20%	-
Kelzan XC	1,800	26	20.5,32.9	100%	1.302
	1,000	40	33,47	100%	1.250
	560	67	64.7,69.4	100%	1.038
	320	-	-	0%	-
Metso Beads	1,000	0.5	-	100%	-
	560	4.0	-	100%	-
	100	-	-	0%	-
Caustic (Celanese)	560	.13	.11,.14	100%	1.064
	320	.33	.31,.35	100%	1.06
	180	6.0	5.2,6.9	100%	1.177
	100	-	-	40%	-
	56	-	-	0%	-

Capryl Alcohol	1,800	0.08	-	100%	1.00
	1,000	0.25	-	100%	1.00
	560	0.50	-	100%	1.00
	320	0.85	0.42,1.71	100%	2.205
	180	0.45	-	100%	1.00
	100	0.9	0.73,1.11	100%	1.262
	56	-	-	0%	-
	32	-	-	0%	-
Tri-Cron	560	4.1	3.85,4.37	100%	1.075
	320	5.1	4.16,6.25	100%	1.257
	180	5.9	4.76,7.32	100%	1.267
	100	13.0	10.7,15.9	100%	1.124
	56	-	-	40%	-
	32	-	-	0%	-
Paraformaldehyde	5,600	0.41	-	100%	1.00
	3,200	0.54	0.52,0.56	100%	1.04
	1,800	1.49	1.46,1.52	100%	1.023
	1,000	2.2	2.1,2.3	100%	1.047
	560	7.9	7.47,8.35	100%	1.065
	320	13	7.5,22.6	100%	1.89
	180	18	12.2,24.5	100%	1.36
	100	39	30,51	100%	1.31
	56	-	-	40%	-
	32	-	-	0%	-
Skot-Free	320	7.8	6.5,9.3	100%	1.225
	180	18	15.5,20.9	100%	1.184
	100	20.5	10.4,40.6	100%	2.200
	56	24.5	20.9,28.7	80%	1.167
	32	-	-	0%	-
Swift's Rig Wash	100	1.5	-	100%	1.00
	56	3.8	3.6,4.1	100%	1.276
	32	23.5	-	100%	1.00
	18	-	-	40%	-
	10	-	-	0%	-

B-Free	56	60.5	46.5,79.0	100%*	1.34
	32	76.	75,77	100%*	1.01
	18	93	84,103	100%*	1.102
	10	103	96,110	100%*	1.08
	5.6	-	-	0%*	-
Dominion Rig Wash	100	1.5	-	100%	1.00
	56	2.9	2.7,3.1	100%	1.086
	32	7.6	7.2,8.0	100%	1.060
	18	50.0	32.5,77	100%	1.663
	10	-	-	0%	-
SS-100	1,000	-	-	0%	-
	100	-	-	0%	-
	10	-	-	0%	-
FLR-100	1,000	-	-	0%	-
	100	-	-	0%	-
	10	-	-	0%	-
Staflo	1,000	-	-	0%	-
	100	-	-	0%	-
	10	-	-	0%	-

*10-day values, not 96 hours.

Appendix B

Experimental Data

Experimental Data Drilling Fluids and Chemicals	Water Hardness, mg/ℓ as $CaCO_3$	Temperature, °C	Acclimation Temperature °C	pH	Dissolved Oxygen mg/ℓ	Number of Fish Per Tank	Average Weight Per Fish, gms	Minimum Weight of Fish, gms	Maximum Weight of Fish, gms	Volume of Test Solution, litres	Test Volume Per Gram of Fish Per Day, based on 4-day exposure	Dates of Starting Tests, 1972
Imperial Rig 51	353	10.2	10.5	8.4-8.95	10-11	5	1.87	1.3	3.3	60	3.2	Sept.16-24
Gulf Rig 15	353	10±0.5	10.5	8.4-8.75	7.1-9.4*	5	1.5	-	-	67.8	2.3	Aug. 21-23
Unlabelled *	353	10.0-10.4	10.5	8.4-8.85	8.0-10.4*	5	1.2	-	-	31.4	1.6	Aug. 18
Unlabelled *	120	10.0-10.4	10.5	8.0-9.95	6.0-11*	4 & 9	1.2	-	-	31.4	1.6	July 22-Aug.8
Gypsum(Plaster of Paris) *	Not	Tested										
Wyoming Bentonite	300	10.5	11.0	8.5	10.5	5	-	-	-	60	-	Sept. 3
CMC - Regular	360	10.7	11.0	8.5	10.5	5	-	-	-	60	-	Sept. 3
CMC - Hi Vis	360	10.7	11.0	8.5	10.5	5	-	-	-	60	-	Sept. 3
Calcium Chloride *		20±1	20±1	7.3-7.8	-	10	-	1.0	9.0	20.4	-	Not Tested*
Aluminium Stearate *	Not	Tested										
Barite *	Not	Tested										
Sodium Bicarbonate *	100	20-22		7.8-8.3								Not Tested*
Torque Trim	360	11.2	11.0	8.5	10.5	5	0.87	0.52	1.12	60	3.45	July 31
Potassium Chloride *	40	20±1	20±1	7.2-9.4	-	10	-	1.0	9.0	20.4	-	Not Tested*
Ferrochrome Lignosulfonate *	355	11.5	11.2	6.7-7.7	11.0	5	0.90	0.53	1.47	60	3.30	Sept. 21
Sodium Acid Pyrophosphate *	370	9.7	10.0	5.5-6.5	11.0	5	1.87	0.99	2.88	60	1.61	Sept. 9
Potassium Chromium Sulfate *	360	11.6	11.2	5.5-7.7	11.0	5	0.49	0.30	0.52	30	3.06	June 26 & Aug.28
Ben-Ex	300	10.5	10.3	8.2	11.5	5	0.80	0.50	1.07	60	3.75	Oct. 16
Kelzan-XC	300	10.5	10.3	8.2	11.0	5	1.00	0.63	1.85	60	3.00	Oct. 16
Caustic (Celanese) *	360	11.5	11.2	8.5->10	11.0	5	1.47	0.86	2.10	60	2.04	July 6 & Aug.28
Capryl Alcohol	380	11.6	11.1	8.5	11.0	5	1.29	0.58	2.08	60	2.33	Aug. 22
Tricron	355	11.0	10.5	8.5	11.0	5	1.27	0.63	1.95	60	2.36	July 25
Paraformaldehyde	340	11.4	11.2	8.5	11.0	5	0.62	0.32	0.87	30	2.41	Sept.21 & 27
Skot-Free	365	10.6	10.5	8.5	11.0	5	1.15	0.67	1.55	60	2.61	Aug. 1
Swifts Rig Wash	300	10.8	10.3	8.2	11.5	5	1.05	0.67	1.75	60	2.86	Oct. 16
B-Free	360	11.0	10.6	8.5	11.0	5	0.57	0.32	0.92	60	5.26	July 11 & 21
Dominion Rig Wash	300	10.4	10.1	8.3	11.0	5	0.97	0.44	2.12	60	3.04	Oct. 24
SS-100	300	10.7	11.0	8.3	11.0	2	0.97	-	-	15	1.93	Nov. 7
FLR-100	300	10.7	11.0	8.3	11.0	2	0.75	-	-	15	2.50	Nov. 7
Staflo	300	10.7	11.0	8.3	11.0	2	0.75	-	-	15	2.50	Nov. 7
Metso Beads	300	10.7	11.0	8.3->10	11.0	2	1.16	-	-	15	1.16	Nov. 7

*See the text of the Results for explanation of special circumstances.