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HAZARDS OF MARINE TRANSPORTATION OF LIQUID CHLORINE

BY

U. S. Department of the Interior
Bureau of Mines
Pittsburgh, Pennsylvania

- Final Report
- March 1970

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The Bureau of Mines has carried out a program of tests in which liquid chlorine was spilled onto a water surface and gaseous and liquid chlorine were released underwater. The scale of experiments ranged up to a 10-gallon (130 lb.) spill and to a 72 lb/hr leak rate under 15 feet of water. Rates of chlorine evaporation were observed photographically and the atmospheric dispersion of the toxic gas was followed by gas sampling. A concurrent laboratory-scale investigation was made of the rates of solution of gaseous chlorine in tap water, cold tap water, and brine. The enlargement of a pinhole during the underwater leakage of chlorine was also observed.

Details of illustrations in
this document may be better
studied on microfiche.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Chlorine Spills on Water						
Evaporation-Chlorine						
Dispersion in Atmosphere						
Gaseous Chlorine						
Toxic Gas						
Underwater Release						
Rate of Solution						
Poison Gas						
Marine Transport of Chlorine						
Chlorine Corrosion						
Chlorine Leak Rate						
Rate of Vaporization						
Air Pollution						
Heavy Gas Layering						

FINAL REPORT

HAZARDS OF MARINE TRANSPORTATION OF LIQUID CHLORINE

March 1970

Prepared by:

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Parameters in the atmospheric dispersion equation (p. 6)

C = concentration of chlorine dimensionless

Q = release rate of gaseous chlorine, ft^3/sec

$\bar{U}$ = mean wind speed, ft/sec

x = downwind distance, feet

y = crosswind distance, feet

z = vertical distance, feet

σ = standard deviation

σ_x, σ_y, σ_z = standard deviation as measured from a plot of concentration vs distance, ft

σ_θ = standard deviation of wind direction, degrees

A, B_2, B_1, C, D = gustiness classifications defined by Table 2.

HAZARDS OF MARINE TRANSPORTATION OF LIQUID CHLORINE

FOREWORD

This report was prepared by the Pittsburgh Mining and Safety Research Center of the U. S. Bureau of Mines as the concluding item of a supporting investigation for the Hazardous Materials Division of the U. S. Coast Guard. Experimental work was conducted from April through December 1969. Six monthly letter reports were submitted and a briefing was performed at Coast Guard Headquarters on December 9, 1969.

The work was performed under the cognizance of W. E. McConnaughey of the Hazardous Materials Division and was administered at Pittsburgh by R. W. Van Dolah. Participating investigators were D. S. Burgess, J. N. Murphy, M. E. Harris, H. Lang, R. Mattes, H. Grainger, W. B. Slomski, and W. Albaugh.

This report was submitted on March 11, 1970, and has been reviewed and approved.

HAZARDS OF MARINE TRANSPORTATION OF LIQUID CHLORINE

Final Report

ABSTRACT

The Bureau of Mines has carried out a program of tests in which liquid chlorine was spilled onto a water surface and gaseous and liquid chlorine were released underwater. The scale of experiments ranged up to a 10-gallon (130 lb) spill and to a 72 lb/hr leak rate under 15 feet of water. Rates of chlorine evaporation were observed photographically and the atmospheric dispersion of the toxic gas was followed by gas sampling. A concurrent laboratory-scale investigation was made of the rates of solution of gaseous chlorine in tap water, cold tap water, and brine. The enlargement of a pinhole during the underwater leakage of chlorine was also observed.

Major conclusions follow:

1. The rate of vaporization of chlorine is very fast; no evidence was found of a rate-limiting heat transfer across a gas film.

2. Contact with water removes a significant fraction of the chlorine in slow leakage or in small spills; it could hardly be a factor in catastrophic accidents.

3. The leak rate of gaseous chlorine through a hole (underwater) in ASTM A-516 Grade 70 steel is markedly accelerated by corrosion.

4. Toxic cloud concentrations downwind of a chlorine release are predictable by existing air pollution equations if one makes appropriate correction for heavy gas layering.

I. INTRODUCTION

The Bureau of Mines has conducted a supporting investigation for the U. S. Coast Guard of the hazards of marine transportation of liquid chlorine. This project was prompted by an application to license for entry into American waterways an ocean-going ship designed to carry several 3,000-ton chlorine tanks.

The program was expected to add to a published review of toxic hazards by the Chlorine Institute[1] by paying particular attention to the spillage or leakage of chlorine into water. Some specific questions were raised in advance[2] of the experimental undertaking: What is the vapor generation rate on spillage of liquid chlorine into water; to what extent is chlorine dissolved on bubbling through water; how is the chlorine leak rate from a submerged tank affected by corrosion; is the toxic cloud concentration reduced significantly on passage over an extended water surface; how does gas layering affect the applicability of micrometeorological equation for cloud dispersion.

The Bureau's work consisted of exploratory experiments which were begun in May 1969 and concluded in December 1969. The scale of tests ranged up to the spillage of 10 gallons of liquid chlorine on a water surface and to the instantaneous release underwater of 5 gallons of chlorine. As the program developed, several of the objectives were found to be of rather academic interest and were accordingly modified; thus, the rate of chlorine vapor evolution was found to be effectively instantaneous when liquid was spilled into water and attempts to measure this rate was therefore discontinued. The greatest part of the experimental effort was related to the downwind dispersion of chlorine concentration. This is reflected in the emphasis given to dispersion phenomena in the sections that follow.

II. ACKNOWLEDGEMENTS

Many persons took a helpful interest in this work and supplied information that would otherwise have been difficult to obtain. We are particularly grateful to Messrs. H. H. Fawcett of the National Research Council, R. Mitchell of the Chlorine Institute, J. A. Clapperton and A. E. Howerton of PPG Industries, W. J. Lawson of Allied Chemical Corporation, G. E. Heym of Mundo Gas, and J. B. Diggory of ICI Limited.

Our larger tests were made possible by courtesy of the Weirton Ice and Coal Company who permitted our use of an isolated lake on their strip mine site near Florence, Pennsylvania.

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[1] A. E. Howerton, "Estimating Area Affected by Chlorine Release," Preprint 27B, Symposium on Loss Prevention in the Process Industries III, Sixty-fourth National Meeting, AIChE, New Orleans, La., March 16-20, 1969. Also, v. 3, Loss Prevention, pp 48-53, a Chemical Engineering Progress Technical Manual, AIChE.

[2] Letter of February 20, 1968, from R. W. Van Dolah to Commandant, U. S. Coast Guard, Attn.: Mr. W. E. McConnaughey.

III. REVIEW OF SOME PERTINENT LITERATURE

The literature on toxic gases, and particularly on chlorine, is voluminous. The few references which are cited below do not constitute an exhaustive review but were chosen to introduce the problem areas on which our work has some bearing.

The critical concentrations of chlorine for various physiological effects are derived largely from some very old literature[3/], most of it related to gas exposures in World War I. The exposure limits from three sources[4,5,6/] are listed in Table 1. It is apparent that critical concentrations should increase with decreasing time of exposure, but no justification could be found for assuming that the dosage (concentration x time) is constant for any level of injury. This poses a certain difficulty in that the readily calculable result of a catastrophic accident is likely to be the dosage, rather than the concentration, of chlorine.

A convenient calculation of toxic gas concentration downwind of a steady ground level source is based on the Gaussian plume model as described by Gifford[7/] and Cramer[8/]. The concentration is

$$C_{(x,y,z)} = \frac{Q}{\pi\sigma_y\sigma_z\bar{U}} \exp - \frac{1}{2}\left[\frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right] \qquad (1)$$

[3/] A. C. Fieldner, S. H. Katz, and S. P. Kinney, "Gas Masks for Gases Met in Fighting Fires," U. S. BuMines Technical Paper 248, 1921.

[4/] Dow Chlorine Handbook (1966).

[5/] Tech. & Eng. Service Bull. 7, Ind. Chem. Div., Allied Chemical Corp.

[6/] F. A. Patty, editor, "Industrial Hygiene and Toxicology," Vol. II, Interscience Publishers (1963).

[7/] F. A. Gifford, Jr., "Use of Routine Meteorological Observations for Estimating Atmospheric Dispersion," Nuclear Safety, v. 2, 47-51 (1961). Also D. Bruce Turner "Workbook of Atmospheric Dispersion Estimates," Public Health Service Publication No. 999-AP-26 (1969).

[8/] H. E. Cramer, "Engineering Estimates of Atmospheric Dispersion Capacity," Industrial Hygiene Journal, 183-9, June 1959.

TABLE 1. - Physiological Effects of Exposure to Chlorine in Air

Effect	Chlorine, ppm		
	4/	5/	6/
Detectable odor	3.5	3.0 to 3.5	-
Throat irritation	15.1	10 to 15	3 to 6
Coughing	30.2	30	-
Dangerous, 1/2 hour	40 to 60	40 to 60	14 to 21
Unbearable, 1 minute	-	-	100
Fatal			
60 minutes	-	-	650 (dogs)
30 minutes	-	1000	300 (cats)
10 minutes	-	1800	-
few deep breaths	1000	-	1000 (large animals)

C = concentration of pollutant, mole fraction

Q = release rate, ft^3/sec

σ = standard deviation as derived from a plot of concentration vs distance, ft

$\overline{U}$ = mean wind speed, ft/sec

x = downwind distance, ft

y = crosswind distance, ft

z = vertical distance, ft

Equation (1) is fulfilled whenever the distribution of chlorine concentration in the y and z directions is Gaussian, with standard deviations σ_y and σ_z, respectively. We have made frequent use of tabulations of σ_y and σ_z compiled at the Brookhaven National Laboratory.[9/] Table 2 comprises some representative information; note that most atmospheric conditions can be approximated by using one set of σ values for the B_1 (unstable) condition and another set of σ values for the D (stable) condition. The maximum concentration as found at ground level on the centerline of air flow ($y = z = o$) is given simply by

$$C = \frac{Q}{\pi \sigma_y \sigma_z \overline{U}} \ . \qquad (1a)$$

In experimental work, one can hold Q very steady over such a time interval as 10 minutes during which the statistical quantities σ_y and σ_z approach the values given in Table 2. Since the denominator of equation (1a), $\pi \sigma_y \sigma_z \overline{U}$, has the units of ft^3/sec and Q represents a steady flow in ft^3/sec, C is properly dimensionless, as for example, parts per million, ppm. But in real accident situations, the chlorine is likely to be evolved as a "burst," as from an exploding reservoir; then Q has the dimensions of ft^3 and C has the dimensions of dosage, for example, ppm sec. Equations (1) and (1a) remain valid if one still has a Gaussian distribution of concentrations (see p. 37 of "Workbook of Atmospheric Dispersion Estimates[7/]"). However, two new problems appear:

[9/] I. A. Singer and M. Smith, "Atmospheric Dispersion at Brookhaven National Laboratories," Air and Water Pollution International Journal, 1966, v. 10, pp 125-135.
M. E. Smith and I. A. Singer, "An Improved Method of Estimating Concentrations and Related Phenomena from a Point Source Emission" Journal Applied Meteorology, v. 5, pp 630-9 (1966).

TABLE 2. - Some Representative Atmospheric Conditions*

Gustiness Classification	Frequency of Occurrence	Average Wind (fps)	Plume Dimensions, ft. σ_y	σ_z
A extremely unstable	1	6	-	-
B_2 unstable	3	12	$0.45\ x^{0.91}$	$0.46\ x^{0.91}$
B_1 unstable	42	23	$0.42\ x^{0.86}$	$0.39\ x^{0.86}$
C neutral	14	35	$0.42\ x^{0.78}$	$0.29\ x^{0.78}$
D stable	40	-	$0.44\ x^{0.71}$	$0.087\ x^{0.71}$

*As observed at the Brookhaven National Laboratory.

(a) As the chlorine moves downwind in an expanding "puff" of diminishing concentration, it is free to disperse in the x (longitudinal) direction as well as in the crosswind and vertical directions. Equation (1) gives the dosage of chlorine received at some location downwind but the concentration of chlorine is not simply the dosage divided by its duration of release. This matter is discussed in Section VI e, below.

(b) The values of σ_y and σ_z which pertain to the expanding puff are not necessarily those given in table 2. For time intervals less than 10 minutes, one may use an approximation[9]

$$\frac{\sigma_y\ (t)}{\sigma_y\ (10\ \text{min})} = \left(\frac{t}{10\ \text{min}}\right)^{0.2} \qquad (2)$$

Over a duration t, of 20 seconds, σ_y has a value about half as large as that given in table 2. One must be careful to recognize that t is not the duration of chlorine release but the duration of dispersion, $x/\bar{U}$. With a 6 mph (9 ft/sec) wind, t is less than 10 minutes for distances, x, up to a mile.

Values of Q to be used in equation (1) have been calculated by the Chlorine Institute task force[1] and are accepted here as authoritative. Figures 1-4 have been reproduced by permission. Figures 1a, b, and c show representative liquid and vapor discharge rates resulting from various modes of tank failure. Note that 1, 5, and 10 pounds/sec or 5, 25, and 50 ft^3 (STP) of gaseous chlorine per second are representative. Based on these values of Q, reference 2 shows the calculated dimensions of toxic gas zone in a 5 mph wind (see figure 2 in which the outer curves enclose 35 ppm concentrations). The effect of heavy gas layering on the dispersion of the toxic cloud was apparently not considered.

In the event of a catastrophic accident, a tank may rupture exposing its contents immediately to atmospheric pressure. Some part of the chlorine must flash-vaporize, cooling the remainder to the boiling point. From consideration of the heat capacity of liquid chlorine and its heat of vaporization (as given, for example, in reference 4), one calculates the fraction of the tank's contents that is immediately evolved (flashed) as a function of its initial temperature (see figure 3). It is pertinent to note that no assumption as to heat transfer is involved in figure 3. The heat of vaporization for the evolved gas is supplied by cooling the residual liquid from its initial temperature to its boiling point. The figure bears on the relative safety of transporting chlorine in refrigerated tankage. At an initial temperature of 100° F, about 22.5 percent of the chlorine is flashed. Thus, in a 55-ton tank at 100° F, Q is about 25,000 pounds or 125,000 ft^3 of chlorine. Figure 4 shows the downwind dispersal of this burst of gas; note that times are well in excess of 10 minutes so that equation (1) may be used legitimately; reference 1 does not make clear how the dosages that derive from equation (1) were converted to concentrations.

With refinements derived from our present experiments with chlorine-water interactions, we think the above information will suffice to calculate the hazardous zone downwind of an accident. It does not answer the larger question "what level of accident probability is safe enough?" The literature on this subject is uniformly interesting[10,11,12] but only one author that we know of has suggested quantitative relationships.[10] His conclusions follow: (1) People will accept a risk voluntarily if it does not seem to them to be much greater than their risk of natural death by disease, that is, about one fatality per 10^6 man-hours of exposure. (2) The same people reject a risk which is imposed on them by their environment and which seems to them to be worse than about 1/1000 of the above, that is, more than one fatality per 10^9 man-hours of exposure. (3) People will accept voluntary risks proportional to the third power of derived benefits; thus, workmen might accept eight-fold greater risk by reason of a doubled pay scale; on the other hand, halving a risk is not likely to appease the person exposed.

The case histories of accidents have not been very informative for us, either because the meteorological conditions or terrain were unspecified or because the population of the environment was not stated. Thus one paper[13] describes the tankage failures releasing:

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[10] Chauncey Starr "Social Benefit versus Technological Risk" Science 165, 1232-8 (1969).

[11] J. M. Brown, "Probing the Law and Beyond: A Quest for Public Protection from Hazardous Product Catastrophes." Staff Discussion Paper 402, Program of Policy Studies in Science & Technology, The George Washington University, Washington, D.C., July 1969.

[12] Paul King "A Systems Approach to Transportation of Hazardous Materials" pp 17-22 of "A Study of Transportation of Hazardous Materials." Contract No. DOT-08-A9-106. National Acad. Sciences--National Research Council.

[13] H. Hennig "Behavior of Gas Clouds in Case of Accidents" Chemiker-Teitung 76, 256-9 (1952).

15 tons of liquid chlorine (7 dead, 200 "poisoned"); 12 tons of phosgene (11 dead within 2,000 meters, 130 non-fatally injured beyond 2,000 meters); and 15 tons of ammonia, accompanied by ignition (15 dead, 20 injured). In each case we have failed to determine how equation (1) could be applied to this experience. The paper's chief conclusion is that persons near a potential gas release should be better educated: To stay inside buildings, closing doors and windows; to flee crosswind rather than downwind to minimize exposure.

Finally, the Bureau's recent study of LNG spillage on water[14] has suggested some factors which should be added to the treatment of reference 1:

1. A liquid like chlorine, which forms a hydrate with heat release should vaporize much faster when spilled into water than when spilled into a diked confinement on land.
2. Since evaporating LNG (density about 1.4 relative to air) produces a heavy surface layer with little vertical mixing, evaporating chlorine with a density at least 2.5 relative to air should also give significant layering.
3. Since peak concentrations downwind of LNG spills were as much as 20 times higher than time-average concentration given by equation (1), similar peak concentrations are to be expected with chlorine.

IV. EXPERIMENTAL PROCEDURES

A. Procedures with Gaseous Chlorine

1. The Rate of Solution of Gaseous Chlorine in Water (Laboratory Tests)

The experiments used to obtain mass transfer coefficients were conducted in a 1-foot diameter by 5-foot tall glass tank (figure 5). Chlorine gas was bubbled through 1/4-inch stainless steel tubing that extended below the water surface to depths of 4.5, 2.0, and 1.0 foot. A glass wool flowmeter, calibrated with a soap film meter, was used to obtain flowrates of chlorine between 25 and 300 cc/min. The tank was filled with 26 gallons of non-chlorinated water at room temperature or at 7° C, or with 2.3 percent brine. Above the water interface was a head space of about 4,000 cc through which air flowed at a controlled rate of

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[14] D. S. Burgess, J. N. Murphy, and M. G. Zabetakis, "Hazards Associated with the Spillage of Liquefied Natural Gas on Water" Bureau of Mines R.I. 7448, November 1970, 27 pp.

1,000 cc/min. A 1/4-inch stainless steel sample outlet was positioned about 1/4 inch above the water surface and was connected to a glass sample train containing eight petticoat bubblers. The solution in each bubbler consisted of 5 cc of starch indicating solution, increasing amounts of 0.025N or 1N sodium thiosulfate solution, and enough 2 percent or 5 percent potassium iodide solution to make a total volume of 50 cc.

Chlorine was initially bubbled through the water at a flow rate of 30 to 50 cc/min and the undissolved chlorine which emerged from the water was swept into the first bubbler. The color change of the bubbler solution to blue was timed and then the sample flow was vented into the hood. The flow of chlorine into the water was increased and the air stream was passed into the second bubbler until a color change was observed and timed. This process of venting, increasing flow rate, and timing of color change was repeated for the eight bubblers. Sodium thiosulfate solution was added to each bubbler until the solution turned colorless. The volume of chlorine gas absorbed in each bubbler was determined by the fact that 1 ml of 0.025N sodium thiosulfate solution is equivalent to 0.31 cc of chlorine at laboratory temperature and atmospheric pressure of chlorine.

In each test the rise time of a bubble was determined by stopwatch or by motion picture photography. Still photographs gave the number of consecutive bubbles in the tank at each flow rate, thus the number of bubbles per minute of chlorine gas. Combining the number of bubbles per minute with the measured chlorine flow rate gave the volume of chlorine per bubble and the equivalent radius.

The curve in figure 6 shows the rise rate of air bubbles in distilled water as a function of bubble radius[15/] the shape of the curve is apparently quite typical. Small bubbles, up to about 0.1 cm radius, at the left of the figure, are spherical and, therfore, most easily studied but probably of no great practical importance in this program; chlorine bubbles of this size should dissolve within a short distance of their formation. Bubbles of about 0.1-0.5 cm radius are generally oblate spheroids and have one favorable characteristic that their rise rates are not changed very much as the gas dissolves and the size of the bubble decreases. The continuous bubbling of chlorine at 4.5, 2.0, and 1.0 feet produced bubbles of this shape and equivalent radius. Our measured rise rates are in good agreement with the curve in figure 6.

Bubbles of greater than about 0.3-0.5 cm (equivalent) radius are usually described as "spherical caps." This was the type that

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[15/] Haberman, W. L., and R. K. Morton. An Experimental Investigation of the Drag and Shape of Air Bubbles Rising in Various Liquids. David Taylor Model Basin, Report 802, NS 715-102, Sept. 1953.

occurred when the apparatus was modified to generate single bubbles of about 10, 30, and 50 cc initial volumes. A 50 cc glass beaker was inverted above the bubbler at a depth of 2 feet by a flexible cable drive which enabled the beaker to be rotated through 180 degrees. Chlorine gas was bubbled into the inverted beaker to displace water to the volume desired and then released as a single bubble by rotating the beaker to an upright position.

Spherical cap bubbles are difficult to study because of their fluctuating shapes and surface/volume ratios but they do have the interesting characteristic that their rise rate is strictly a function of size, being independent of fluid properties. For air in many liquids

$$\text{Rise rate, } U = 1.02 \sqrt{g\, r_e} \qquad (3)$$

where g is the gravitational constant and r_e the equivalent radius. Our measured rise rates of spherical cap bubbles are given in fair approximation by figure 6 or equation 3.

2. Atmospheric Dispersion Tests of Gaseous Chlorine and Butane (Bruceton pond)

Butane was used as a reference gas because it is nearly as dense as chlorine and sparingly soluble in water. Its flow was controlled in the liquid phase by a Kates regulator after which it was allowed to vaporize in copper tubing. Chlorine flow was controlled in the liquid phase with a stainless steel needle valve and the supply cylinder was supported on a balance for periodic reading of weight loss. The two gas outlet lines were suspended about 3 inches above the water surface and 3 feet apart so that considerable dilution with air had occurred before the gas streams mixed.

In order to determine the atmospheric dispersion of the chlorine and butane, an array of eleven sampling systems was located on the pond and on the shore line downwind of the steady gas sources (figure 7). A floating rig formed a 102° arc of a 50-foot radius circle with the gas sources located at its center. Six bubblers were located on the rig, four along a horizontal and two in a vertical array of one and five feet above the water. Five bubblers were located on the shore line at an average distance of 135 feet from the gas source. A wind speed and direction transducer was located on a barge downwind of the bubblers.

Each bubbler was connected to a 10-liter evacuated sample bottle with an orifice inlet requiring 20 minutes or more to bleed to atmospheric pressure. Curves of sampling rate for the fastest and slowest orifices of the eleven used are shown in figure 8. The curves are linear for pressures to one-half atmosphere as expected if sonic velocity was obtained in the orifices used. Indeed, during the 10-minute duration of a dispersion test the curves are essentially linear.

The chlorine plus butane-air samples were pulled through the bubblers where chlorine was removed from the sample by reaction with the potassium iodide solution and the remaining sample of butane was collected in the 10-liter sample bottles. Butane concentrations were obtained by a gas chromatographic-flame ionization procedure and the chlorine contents of the bubblers were determined as previously described.

B. Spillage of Liquid Chlorine

In order to obtain an order of magnitude observation of the vaporization rate of liquid chlorine spilled onto water and to observe the penetration of the dense liquid chlorine ($\rho = 1.47$) under the water, several spills were conducted in which 0.75 gallon of chlorine was rapidly poured into a one-foot diameter by 4-foot deep glass pipe filled with water. The event was observed with a 64 frame/sec movie camera. The event lasted less than a second during which time the chlorine was flash-vaporized leaving a considerable quantity of chlorine hydrate on the water surface. The penetration of the water by the chlorine was only 8 or 10 inches. Due to the rapidity of gas evolution it was impossible to measure vaporization rate as originally planned.

Several large-scale spills (up to 10 gallons of liquid chlorine) were conducted on open water at the strip mine lake. The chlorine was contained in an open-mouth polyethylene-lined and insulated container; the container was suspended one foot above the water and remotely emptied by using explosive-activated cable cutters permitting the container to rapidly invert in about one second. The experiments were observed with 128 and 24 frame/sec cameras. (See figure 9.)

The underwater release of liquid chlorine was accomplished as follows:

The chlorine was contained in 1- and 5-gallon glass bottles which were insulated with a 1-inch layer of polyurethane foam; the insulated bottle was then covered with a 5-mil polyethylene bag to exclude water; a vent hose was provided to avoid pressure buildup; the filled containers were suspended by a cable over the center of the lake, submerged, and then ruptured with two number 8 electric blasting caps which shattered the glass container but minimized the dispersion of liquid chlorine. The emergence of the chlorine gas bubbles on the surface was observed with high-speed motion pictures (figure 10) and the concentration of the chlorine-air cloud downwind was monitored along the shore line at 50-foot intervals with six of the bubblers and evacuated sample bottles discussed above. A schematic of the lake and location of the sampling stations is shown in figure 11. The distances from the release to the shore line was 100 to 270 feet.

C. Corrosion Tests

Several experiments were conducted to determine the effect of corrosion on a chlorine leak in a steel tank underwater. Using the steel that chlorine tanks are fabricated from (ASTM A-516) a pinhole leak in a 5/8-inch thick steel container was simulated by a 0.030-inch diameter hole as shown in figure 12. Liquid or gaseous chlorine was flowed through the hole and the mass flow rate of chlorine was observed to determine if the leak was enlarging. The block was submerged under about 15 feet of water and positioned so that the major axis of the hole was horizontal. Gaseous chlorine was released through the hole at 10 or 90 psig back pressure for up to four hours and liquid chlorine at its own vapor pressure for two hours. The blocks were subsequently examined for increase in the diameter and volume of the orifice.

V. EXPERIMENTAL RESULTS

A. Solution of Gaseous Chlorine in Water and Brine

The percentages of chlorine dissolved in water at room temperature and at 7 °C, and in brine with 2.3 percent sodium chloride are given in figure 13 as function of flow rate and of liquid depth. As expected, the percentage of chlorine dissolved is higher in cold water than in water at room temperature and lower in brine than in water. At a depth of 4.5 feet of water almost all the chlorine was removed before the bubbles reached the surface. Visually it was noted that the oblate spheroid bubbles of 0.3-0.4 cm equivalent radius formed at the 4.5-foot depth did not vanish but tended to become ore spherical in shape as they rose and by the time the surface was reached were very small. The volume of a gas bubble which consists of a gas soluble in water, such as chlorine, will decrease considerably but not vanish completely while floating up because the diffusion of air from the water into the bubble takes place simultaneously with diffusion of chlorine into the water.

The standard equation for the mass transfer rate per unit surface area is

$$-\frac{dN}{dt} = K_L A \, (C^* - C_L) \qquad (4)$$

where the mass transfer coefficient, K_L, is the quantity of interest for generalizing laboratory data to situations of practical importance. By typical transformations as detailed in reference 13, one obtains

$$K_L = -\frac{1}{HRT}\left[\frac{1}{A}\frac{dV}{dt} + \frac{V}{A}\frac{1}{Z + Z_B}\frac{dZ}{dt}\right] \qquad (5)$$

Equation (5) shows that the mass transfer coefficient may be calculated from values of bubble volume, V, bubble area, A, and liquid head, Z, as functions of time.

When K_L was derived from the experimental data of figure 13 and equation (5) the values were in quite good agreement with reported values in reference 12 for CO_2 (see figure 14). Thus, by equation (4), the rates of solution of chlorine and CO_2 are in direct proportion to their equilibrium solubilities which differ by a factor of 3.

The "aging" of bubbles by which K_L decreases with increasing length of path is apparent from figure 14. The ingenious theories to account for this effect are not pertinent here but a related empirical observation is useful.[16]

$$\frac{\int_0^t K_L \, dt}{t} = \bar{K}_L \propto Z^{-1/3} \qquad (6)$$

where $\bar{K}_L$ is the average transfer coefficient throughout the lifetime of the bubble and Z the height of water column. Figure 15 shows the straight line on a logarithmic scale for air bubbles from reference 13 along with points for CO_2 from reference 12 and our points for chlorine.

In reconsideration of the above work, it was decided that further study of solution rates would not be rewarding. To have shown that K_L was nearly the same for chlorine as for CO_2 and air is equivalent to

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[16] Eckenfelder, W. Wesley, Jr., and Edwin L. Barnhart. The Effect of Organic Substances on the Transfer of Oxygen from Air Bubbles in Water. AIChE Jour., v 7, No. 4, pp 631-34.

proof that the hydrolysis of chlorine and subsequent ionization are second-order effects; also that the common ion effect of dissolved sodium chloride should have little effect on rates of solution (compare figure 13). The key question as to solubility is the flow rate at which bubbles coalesce and a "channel" forms by which chlorine escapes upward through the water; this is discussed in Section VI, F, below.

B. Corrosion Tests

The effect of gaseous chlorine at 10 psig flowing through a 0.030-inch diameter x 0.625-inch long hole in a block of ASTM A-516 Grade 70 steel submerged under water, is shown in figure 16. The mass flow rate as a function of time as shown in the figure remained constant for approximately three hours, then there was an abrupt four-fold increase in the rate and after another hour there was an additional increase in the flow. A similar phenomena was observed in another experiment with 90 psig gaseous chlorine except for the higher initial flow rate and the reduced time interval between flow changes as shown in figure 17. Subsequent examination of each hole after the experiment indicated that the original opening was enlarged initially from the outside and the opening had the form of a truncated cone.

In figure 18 the original block and the results after the experiment with gaseous chlorine described in figure 17 are shown. In each case the hole was enlarged to approximate the shape of a truncated cone with a limiting orifice near the inside of the hole. When the corrosion removed the orifice the flow increased as shown in figures 16 and 17.

An additional experiment was conducted in which liquid chlorine at 90 psig was discharged through an orifice under water. The results are shown in figure 19. For several minutes the flow was rather high (about 70 lb/hr) but rapidly decreased and held at 3.4 lb/hr for approximately 45 minutes. When the flow again increased to 72 lb/hr numerous large ice or hydrate floes periodically came to the surface of the water; when the flow rate decreased no ice was observed. There was no appreciable corrosion of this particular orifice. The results of the experiments are summarized in table 3 where the results are expressed as the change in volume of the hole since the irregular shape of the corroded holes prevent accurate description of the dimensions.

TABLE 3. - Effect of the exposure of ASTM A-516 steel to chlorine in an aqueous environment

Chlorine	Pressure (psig)	Hole Volume (cc) Initial	Hole Volume (cc) Final	Time (hours)
Gaseous	10	7.25×10^{-3}	7.9×10^{-2}	4
Gaseous	90	7.25×10^{-3}	23.7×10^{-2}	2
Liquid	90	7.25×10^{-3}	9.0×10^{-3}	1.75

In the case where the liquid chlorine did not appreciably affect the steel, it appears as though the vaporizing chlorine at the orifice freezes the water and the ice retards the flow; eventually, the ice breaks away and the flow is momentarily increased.

No attempt was made to investigate the corrosion effect of chlorine on other materials such as valves and fittings.

C. Atmospheric Dispersion of Chlorine and Butane Over Water

Much consideration went into the choice of a reference gas which would have about the same density as chlorine and which might be used for shaking down the experimental procedures. It was desirable that this gas be sparingly soluble in water so that a comparison between atmospheric concentrations of chlorine and concentrations of the reference gas would indicate any alleviation of chlorine concentration by its solubility in water. Finally, it was necessary that the reference gas be susceptible to analysis in the range of tenths of a part per million. The best choice appeared to be butane, the pertinent characteristics of which are given in table 4.

Test #1

The objective of this experiment was to test the dispersion of a heavy gas for comparison with our recent results using LNG. Measured concentrations were to be compared with prediction by equation (1)

$$C_{(x,y,z)} = \frac{Q}{\pi\sigma_y\sigma_z\bar{U}} \exp - \frac{1}{2} \left[\frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right] \qquad (1)$$

for which definitions are given in Section III. In particular, we had found with LNG that heavy gas layering could be accounted for by assigning σ_z a value of 0.2 σ_y.

A steady flow of 0.526 pounds butane per minute was established over an 11.4 minute interval. The average wind velocity as measured 18 inches above the water surface was 2.76 mph and the standard deviation of wind direction, σ_θ, was 47.0°. Taking

$$\sigma_y = x \tan \sigma_\theta \qquad (7)$$

which was well established in the LNG program and assuming

$$\sigma_z = 0.2\, x \tan \sigma_\theta \qquad (8)$$

TABLE 4. - Selected properties of butane and chlorine

	Chlorine	Butane
Molecular weight	70.91	58.12
Density at 25 °C (air = 1)	2.45	2.00
Boiling Point, °C	-35	0
Solubility in water, ml/100 g	310 at 10 °C	15 at 17 °C
Method of Analysis	titration	flame ionization
Nominal sensitivity of analysis, ppm	0.1	0.1

the maximum concentration of butane is calculated at 50 foot distance (x) to be 8 ppm and at 150 feet to be 1 ppm. Table 5 shows experimental and calculated concentrations at the 11 sampling positions.

One experimental concentration, 17 ppm at station 5, was considerably out of line; when this same station gave another high result on the following test, we decided that the sample bottle must have been contaminated in previous usage. For this reason, this one concentration was omitted from the overall average. The experimental average of 7.7 ppm at 50 feet compares favorably with a calculated average of 6.8 ppm; likewise the experimental 0.8 ppm at 135-150 feet is comparable to the calculated 0.9 ppm. Concentrations at individual stations were not so well predicted but this would be asking too much of a test of such short duration.

Test #2

Butane and chlorine were released simultaneously. The chlorine flow was about half that of the butane so that any appreciable reaction between them should show particularly in the chlorine concentrations. Wind direction was unusually variable during this test ($\sigma_\theta = 54.0°$) and predicted concentrations were accordingly lower than in Test #1. Both chlorine and butane averaged about two-thirds their predicted levels at 50 feet downwind (Table 6). At longer distances (110-120 feet), there was one irregularity, an unexpectedly high chlorine concentration at sampling station #9.

A detectable odor of chlorine is associated with 3.0-3.5 ppm (Table 1); two observers reported chlorine odors, presumably the result of peak concentrations, at distances up to 200 feet downwind where the time-averaged level should have been no more than a few tenths of a part per million.

Test #3

Chlorine and butane were released at about the same rate. Wind velocity was somewhat higher than in the previous tests and the standard deviation of wind direction was only 27.7°. Both gases were found in concentrations quite similar to predicted values (Table 7). As one might expect with a steadier wind, concentrations at the individual stations were also quite close to prediction.

TABLE 5. - Dispersion of 0.526 lbs Butane per Minute Over Bruceton Pond (Test #1)

$\overline{U}$, mph	$\overline{U}$, ft/sec	σ_θ, degrees	x, feet	y, feet	z, feet	Butane concentration, ppm	
						Eqn. (1)	Experimental
2.76	4.06	47.0	50	-45	0	5.5	8.8
			50	-15	0	7.5	5.6
			50	15	0	7.5	6.3
			50	45	0	5.5	9.2
			50	0	1	7.9	(17.0)
			50	0	5	7.1	8.8
		Average				6.8	7.7
			150	-70	0	0.8	1.4
			150	-35	0	0.9	0.6
			135	0	0	1.1	1.2
			140	35	0	1.0	>0.0
			150	70	0	0.8	0.1
		Average				0.9	0.8

TABLE 6. - Dispersion of 0.625 lbs Butane per Minute and 0.40 lbs Chlorine per Minute Over Bruceton Pond (Test #2)

$\bar{U}$, mph	$\bar{U}$, ft/sec	σ_θ, degrees	x, feet	y, feet	z, feet	Butane Conc., ppm		Chlorine Conc., ppm	
						Eqn. (1)	Exp.	Eqn. (1)	Exp.
2.82	4.15	54.0	50	-75	0	3.0	1.1	1.6	0.8
			50	-45	0	4.5	2.6	2.4	1.1
			50	-15	0	5.4	4.2	2.9	3.3
			50	15	0	5.4	4.2	2.9	2.4
			50	-30	1	5.0	(21.7)	2.7	0.2
			50	-30	5	4.7	3.7	2.5	2.5
		Average				4.7	3.2	2.5	1.7
			110	0	0	1.2	0.6	0.6	0.8
			110	35	0	1.1	1.0	0.6	0.9
			110	70	0	1.0	1.5	0.6	2.4
			120	-35	0	0.9	0.1	0.5	0.4
			115	-105	0	0.8	0.1	0.4	0.
		Average				1.0	0.7	0.5	1.0

TABLE 7. - Dispersion of 0.338 lbs Butane per Minute and 0.45 lbs Chlorine per Minute Over Bruceton Pond (Test #3)

$\overline{U}$, mph	$\overline{U}$, ft/sec	σ_θ, degrees	x, feet	y, feet	z, feet	Butane Conc., ppm Eqn.(1)	Butane Conc., ppm Exp.	Chlorine Conc., ppm Eqn.(1)	Chlorine Conc., ppm Exp.
3.87	5.69	27.7	50	-75	0	0.3	0.0	2.8	0.5
			50	-45	0	3.4	4.2	3.8	4.3
			50	-15	0	12.6	13.3	14.0	14.5
			50	15	0	12.6	14.1	14.0	11.0
			50	-30	1	9.9	6.8	8.4	6.7
			50	-30	5	4.9	3.5	5.4	5.1
		Average				7.3	8.4	8.1	7.0
			150	-175	0	0.1	0.0	0.2	0.2
			150	-105	0	0.7	0.4	0.8	0.7
			135	-70	0	1.3	0.7	1.4	1.0
			140	-35	0	1.7	1.3	1.9	1.4
			150	35	0	1.5	1.8	1.7	2.3
		Average				1.1	1.1	1.2	1.1

Following tests #1, #2, and #3 it was apparent that steady flows of both chlorine and butane were dispersed in accordance with the Gaussian plume model in which the vertical standard deviation, σ_z, was given approximately by 0.2 σ_y. Since this result conforms to our earlier finding with LNG, no further tests over the present range of distances were considered necessary. Since butane and chlorine gave so nearly the same result, we could find no reason to argue that chlorine was being absorbed significantly at the water surface.

D. Underwater Release of Liquid Chlorine

Test #4

In this experiment, five gallons of liquid chlorine were released underwater by shattering a glass carboy with blasting caps. The primary objective was to observe the phenomenon photographically for such information as the rate of evaporation and evidence of chlorine hydrate. Following the successful results of tests #2 and #3, sampling stations were installed along the shoreline of the lake (figure 11) to observe whether an appreciable fraction of the chlorine had been lost in the water. As it turned out, the gas sampling was more interesting in connection with the use of equation (1) to predict dosages from instantaneous chlorine releases.

The sampling bubblers were set into operation, after which the experimenters vacated the area, the chlorine bottle was lowered underwater and shattered, the gaseous chlorine was dispersed downwind, and finally the experimenters reentered the area to retrieve the bubblers. Thus the sampling continued over a 15-16 minute period which included a short interval of appreciable chlorine concentration.

Titration of the bubbler solutions gave the total amount of chlorine dissolved. From the pressure drop in the 10-liter sample bottles, one knows the volume of chlorine-air flow (see figure 8); therefore the average chlorine concentration over the total 15-16 minute period. This establishes the chlorine dosage (ppm sec) at each station (see table 8).

Since the lake was confined within high, steep banks with a very narrow "beach," wind measurements were not very satisfactory. The wind velocity, 7.3 ft/sec, was judged from motion pictures of the movement of the chlorine cloud. The angular standard deviation, 33°, was obtained by interpolation of figure 20, which comprises our paired measurements of $\bar{U}$ and σ_θ at the Bruceton facility (points) and Brookhaven National Laboratory measurements (solid line) at an elevation of 100 meters. Table 8 shows that calculated dosages using $\sigma_\theta = 33°$ are conspicuously low.

TABLE 8. - Chlorine dosages following underwater release of 5 gallons liquid (Test #4, $\overline{U}$ = 7.3 ft/sec)

Sample Station	x, feet	y, feet	Calculated* dosage, ppm sec	Observed dosage, ppm sec	Calculated** dosage, ppm sec
1	100	-150	1,280	280	5
2	110	-100	5,810	59,500	1,630
3	140	-50	8,120	15,000	19,600
4	180	0	5,700	22,800	20,300
5	225	50	3,440	21,000	10,500
6	270	100	2,170	35,700	5,060

* Using σ_θ = 33° by interpolation of figure 20.

** Using σ_θ = 19° obtained by equation (2).

The obvious shortcoming of the calculation is that σ_y and σ_z in equation (1) relate to time intervals such as 10-60 minutes while the total dispersion time was of the order of $x/\overline{U}$ or about 14-37 seconds or an average of 0.4 min. An equivalent statement is that the chlorine cloud constituted a vapor "trail" rather than a "plume." From equation (2) we judged that σ_θ for this time interval should be about 19°. Using this value a second calculation was made as shown in the final column of Table 8; predicted values are in fair agreement with experimental dosages at sample positions 3, 4, and 5, which spanned the centerline of airflow as judged from motion pictures of the test. The very high dosage at sample position 2 derived from a separate trail of chlorine which was ejected from the release area in the direction of the sampler.

It is obviously impossible to judge from table 8 whether any chlorine has been lost through its solubility in water. The expected 325 ft^3 (STP) of gaseous chlorine should have occupied an initial bubble of 8.5-foot diameter; this could not be confirmed within any tolerable limits from the photographic coverage. As the yellow cloud moved away from the release area, a white patch remained on the water which had an approximate diameter of 22 feet; this residual film broke up and disappeared within about 30 seconds; it presumably contained some chlorine hydrate.

We conclude from Test #4 that most of the chlorine is vaporized "instantaneously" from the release of 65 pounds of liquid under 4 feet of water and that its atmospheric dispersion is contained within a relatively small angle as implied by equation (2).

Test #5

The quantity of liquid chlorine released was 1 gallon (13 pounds) initially contained in a glass jug which was shattered by blasting caps under 10 feet of water. From photographs we estimate that the diameter of the residual white film on the water was 21 feet; thus, a relatively larger fraction of the chlorine must have been tied up as hydrate. Table 9 shows the dosages at the sample positions are significantly lower than in the previous 5-gallon release, even when allowance is made for the 5:1 ratio of quantities released. Roughly speaking, experimental dosages are about an order of magnitude lower than predictions based on the same 19° σ_θ used in Test #4. We conclude that a major fraction of the chlorine was lost, either by hydrate formation or by solution as the cloud was traversing the water surface.

TABLE 9. - Chlorine dosages following underwater release of 1 gallon liquid (Test #5, $\overline{U}$ = 6.1 ft/sec)

Sample Station	x, feet	y, feet	Calculated* dosage, ppm sec	Observed dosage, ppm sec	Calculated** dosage, ppm sec
1	100	-200	155	0	0
2	110	-150	587	207	5
3	140	-100	947	0	974
4	180	-50	783	180	3,520
5	225	0	526	588	3,130
6	270	50	358	0	1,870

* Using σ_θ = 40° by interpolation of figure 20.

** Using σ_θ = 19° as in Test #4.

VI. DISCUSSION

A. Rate of Vapor Generation on Spillage

The motion pictures of liquid chlorine spillage have destroyed several of our preconceived notions of how liquid chlorine should behave in water. First, we see no evidence that chlorine sinks in water when spilled in quantities up to 10 gallons; it seems rather to be strongly buoyed up by the evolving gas. On the other hand, we see no evidence of a gas film separating chlorine and water to make heat transfer a rate-limiting process.

In every experiment there was some obvious formation of a white solid; this solid retained its identity in a stoppered bottle but melted with chlorine release when the bottle was unstoppered; it was assumed to be chlorine hydrate. According to a recent review[17/], chlorine hydrate is a non-stoichiometric compound of cage-like structure comprising up to 8 chlorine molecules in a lattice formed by 46 water molecules. At maximum chlorine occupancy, the heat of formation is about -6.5 kcal/mole of chlorine, somewhat more than enough to vaporize another mole of chlorine (4.9 kcal/mole). We do not know its density but it is presumably closer to that of ice than to that of liquid chlorine. As best we can judge from photographs, the liquid chlorine-water interaction leads to a turbulent mixture of chlorine, water, hydrate, and gas which is sufficiently buoyant that hydrate is ejected into the atmosphere along with gas and possibly droplets of liquid chlorine. In any case, it is a very fast process.

Figure 21 compares the elapsed times for gas cloud evolution in several experiments (points) with computed elapsed times over which a person would be subject to 50 or 500 ppm chlorine in the same size of spill (solid lines). As long as the time of evolution is much less than the subject's exposure time, we can speak of the gas generation as being instantaneous. The derivation of the lines in figure 21 is described in the following section.

[17/] W. C. Child, Jr., "Molecular Interaction in Clathrates; a Comparison with Other Condensed Phases." Quarterly Review 18, 321-46 (1964).

B. Dispersion of an Instantaneously-generated Cloud of Gas

As one follows the cloud of chlorine downwind, the concentration decreases as the boundaries of the cloud increase, as shown in figure 4. The crosswind distribution of concentrations at ground level is shown schematically in figure 22. The measure of cloud dimension is σ_y which is given for typical wind conditions by Table 2. Now it is a fairly good assumption that turbulence is isotropic in a horizontal plane, that is, that the cloud is symmetrical in this plane as assumed in figure 4. In other words, the standard deviation of downwind concentration distribution, σ_x, is equal to σ_y. The area under the concentration vs distance (x) curve is unity if distance is expressed in units of σ_x and the peak concentration is given the normalized value of 0.399. The same area is contained under a rectangular distribution (dashed lines) which is 2.5 σ_x long and 0.399 high.

But the observer in a chlorine-air mixture is not concerned with cloud dimensions in feet but with the cloud duration in seconds. So we define $\sigma_t = \sigma_x/\overline{U}$ as the standard deviation of a concentration vs time curve. The area under this curve (dosage) is equal to the area under a rectangular pulse at peak chlorine concentration lasting for 2.5 σ_t seconds.

$$\text{dosage, ppm sec} = C_{max}\ (\text{ppm}) \times 2.5\ \sigma_t\ (\text{sec}) \tag{9}$$

As an exercise in the use of equation (9) we have calculated peak concentrations in the underwater release of Test #4 (table 10). Since distances were short, we approximate σ_y or σ_x by x tan 19° and divide these numbers by the wind speed of 7.3 ft/sec to get σ_t. The peak concentration is given by the observed dosage divided by 2.5 σ_t. If the experimenters had not vacated the sampling zone they would have encountered a chlorine concentration of the order of 1,000 ppm or higher for an equivalent duration, 2.5 σ_t, of 12.5 to 34 seconds which is probably ample for the "few deep breaths" leading to lethality (table 1).

The reference lines in figure 21 represent 2.5 σ_t at distances where the chlorine concentration is 50 ppm and 500 ppm downwind from various amounts of instantaneous gas release.

Concerning the use of equation (1) to calculate dosages downwind of an instantaneous gas source, Q, we have already shown (table 8) that the usual approximations for σ_y and σ_z are too high when Q is small and the pertinent distances are short. From our

TABLE 10. - Calculated peak concentrations in Test #4

Sample station	x, feet	$\sigma_y = \sigma_x = x \tan \sigma_\theta$ feet	$\sigma_t = \frac{x \tan \sigma_\theta}{\bar{U}}$ sec	Observed dosage ppm sec	Calculated peak conc., ppm
1	100	36.4	5.0	280	22
2	110	40.0	5.5	59,500	4,300
3	140	50.9	7.0	15,000	860
4	180	65.5	9.0	22,800	1,000
5	225	82.0	11.2	21,000	780
6	270	98.3	13.5	35,700	1,100

experience, σ_y and σ_z behave like proper statistical quantities when the observation time is 10 minutes or longer. Thus, if wind speed is 10 ft/sec, the equation should become approximately valid at x = 6,000 ft. In most "catastrophic" situations, the affected distance will be greater than 6,000 feet.

C. Calculation of Gas Concentrations from Steady Sources

Nomographs have been prepared for maximum chlorine concentrations under representative stable and unstable atmospheric conditions. For stable conditions we have used σ_y and σ_z as given for D gustiness in table 2. Substituting these values into equation (1) the ground level, centerline concentration (y = z = o) becomes

$$C = \frac{8.3 \times 10^6}{x^{1.42}} \frac{Q}{\bar{U}} \text{, ppm} \qquad (10)$$

The procedure in using this nomograph (figure 23) is to draw a straight line from the pertinent wind speed, $\bar{U}$, to the pertinent distance, x, intersecting the α-scale; draw a second line from the α-intersection to the pertinent gas release rate, Q, crossing the concentration scale, C, at the resultant parts per million of chlorine. Since C and Q are linearly proportional in equation (10), concentrations may also be estimated for gas release rates that are off-scale in figure 23.

Alternately, one may draw through a known Q and a critical C to a value on the α-scale and then through this intersection value and known $\bar{U}$ to the distance, x, at which the concentration will be found.

For unstable atmospheric conditions we have used σ_y from the B_1 line of table 2 and taken account of layering by setting $\sigma_z = 0.2\ \sigma_y$. Thus the ratio of horizontal and vertical diffusion is assumed to be the same under stable and unstable conditions. Substituting into equation (1), the ground level, centerline concentration for unstable conditions is given by

$$C = \frac{9.0 \times 10^6}{x^{1.72}} \frac{Q}{\bar{U}} \text{, ppm} \qquad (11)$$

A nomograph based on equation (11) is given in figure 24. To illustrate its use, consider the representative leaks of 5, 25, and 50 ft^3/sec suggested by figures 1a, b, and c. Drawing from these Q values through a concentration of 35 ppm to the α-scale and connecting the α-intersections with $\overline{U} = 7.5$ ft/sec, one finds distances of 1100, 2800, and 4200 feet, respectively. On comparing these distances with the outlines of 35 ppm concentration in Figure 2 (unstable conditions), we find that our prediction is far more conservative than the one given by the Chlorine Institute task force.[1] Much of the difference arises because we have assumed layering ($\sigma_z = 0.2\ \sigma_y$). Without layering we would have had 430, 1100, and 1650 feet extensions of the zone containing 35 ppm chlorine. This brings us within an approximate factor of 2 of the predictions in figure 2.

D. The Importance of the Area Covered by a Chlorine Spill

Strictly speaking, equation (1) and other derived equations apply only to a point source of pollutant, such as a smokestack. If a given source of pollutant (equal Q) is spread over an extended area, the resultant plume is somewhat shorter in the (downwind) x-direction and wider in the (crosswind) y-direction. A straight-forward way to calculate the plume from an area source is to divide the area into a number of small subareas and treat each subarea as an independent source; by modern computational methods this is not a formidable problem.

However, it is far simpler to ignore the area of the spill and this section seeks to justify the consideration of chlorine spills in water as point sources of evolved gas.

Let us assume the steady release and evaporation of 10 lbs/sec of chlorine, generating a Q of 50 ft^3/sec of chlorine gas. Using figure 24 with an assumed wind speed of 10 ft/sec one obtains the centerline chlorine concentrations at various downwind distances as given in the second column of table 11. To obtain off-centerline concentrations, one must know σ_y, assumed to be $0.43\ x^{0.86}$, as given in the final column of the table. Equation (1) now permits the calculation of concentrations 50 and 100 feet off-centerline which are given in the third and fourth columns of Table 11.

Now assume that the chlorine flow is divided into four equal flows which are spilled at the corners of a square which is 100 feet on a side (this is a fair approximation to the distribution of liquid chlorine over an acre of water surface). The coordinates (x, y) of the four small spills are now (50,50), (50,-50), (-50, -50), and (-50,50) feet. The chlorine concentrations resulting from each of the four small spills were calculated and added together giving the bracketed numbers in table 11.

TABLE 11. - Concentrations, ppm, downwind of a point source of chlorine gas (unbracketed) and downwind of a distributed source (bracketed)

Downwind Distance, x, ft.	Concentration at y =			
	0	50	100	σ_y, ft
500	1025	865	520	86
	(876)	(782)	(537)	
1000	311	295	253	156
	(296)	(283)	(245)	
2000	95	94	89	282
	(93)	(92)	(87.6)	
4000	27	27	27	513
	(27)	(27)	(27)	

One sees that there is some difference in the bracketed and unbracketed values at 500 feet, a difference that is large relative to the errors of reading a nomograph or a slide rule, but small relative to the uncertainties of wind gustiness classification. At all distances beyond 1,000 feet, the bracketed and unbrackered values are identical within the reading errors of a nomograph such as figure 24.

In general, the dimensions of the spill area are important when these dimensions are large relative to σ_y, as they are in the illustrative example at 500 feet from the assumed spill. Therefore, if chlorine is spilled on land and is caught within a diked area from which it evaporates very slowly, the downwind distance, x, at which one observes significant concentration is short and the dimensions of the impoundment area should be considered. But when chlorine is spilled into water, gas evolution is so fast x and σ_y become very large and the source area is insignificant. In test #4, for example, the apparent area from which chlorine was liberated was a circle of 22-foot diameter while σ_y at C = 1,000 ppm was 40-100 feet. (See table 10)

E. Calculation of Gas Concentrations from Instantaneous Release of Gas

In this problem, the C given by equation (10) or (11) is a dosage, ppm sec, and is related to peak concentration C_{max}, by equation (9). Under stable atmospheric conditions, $\sigma_y = \sigma_x = 0.44\ x^{.71}$ and $2.5\ \sigma_t = 1.1\ x^{.71}/\bar{U}$. Substituting this into equations (9) and (10), one obtains

$$C_{max} = \frac{7.54 \times 10^6\ \ Q}{x^{2.13}}\ , \text{ppm} \qquad (12)$$

with Q expressed as ft^3 chlorine. The nomograph, figure 25, is simpler than those of the previous figures because concentration is independent of wind speed.

The comparable equation for unstable conditions employs $\sigma_x = \sigma_y = 0.43\ x^{.86}$ from table 2; therefore, $2.5\ \sigma_t = 1.08\ x^{.86}/\bar{U}$, and

$$C_{max} = \frac{8.33 \times 10^6\ \ Q}{x^{2.58}}\ , \text{ppm} \qquad (13)$$

The corresponding nomograph appears in figure 26.

To illustrate its use, consider the rupture of a 55-ton tank car of liquid chlorine at an initial temperature of 100° F. According to figure 3, about 22.5 percent of the liquid should vaporize quickly, giving Q - 125,000 ft^3 (STP) of gaseous chlorine. If one wishes to know the distance at which one would observe 35 ppm chlorine, one notes that C and Q are directly proportional in equation (13); therefore, the relevant distance is unaffected if one divides both C and Q by a constant, say 1,000; drawing a line from 125 ft^3 through 0.035 ppm, one finds a distance of 12,000 feet. This distance pertains either to a 0.035 ppm concentration from a 125 ft^3 source or to a 35 ppm concentration from a 125,000 ft^3 source. The agreement with the Chlorine Institute calculation (figure 4) is very good.

F. Effectiveness of Water in Alleviating Chlorine Releases

If a submerged tank of chlorine develops a pinhole leak on its upper surface so as to emit a slow series of gas bubbles, figure 13 shows clearly that most of the chlorine will be dissolved within a few feet of rise path. But the same figure also shows that the undissolved fraction is increasing as the flow rate is increased and the bubbles are spaced closer together; from 1 to 10 percent of this initial chlorine is passing through 4-1/2 feet of water at a bubble input rate of 250 cc/min, which comprises 825 bubbles/min. At this flow rate, 69 consecutive bubbles can be counted in a photograph of the 4-1/2-foot (137 cm) path. Thus the center-to-center spacing is 2.0 cm and the initial bubble diameter 0.84 cm. If the bubble frequency is further increased without changing the bubble diameter, the bubbles should start to touch and coalesce at about 600 cc/min; if the bubble diameter is increased without changing the center-to-center spacing at a flow of 3,000-4,000 cc/min. In fact, somewhat higher flows than these could occur without "channeling" because large bubbles develop a spherical cap shape (see figure 27) and do not rise in a straight line.

In the corrosion tests, chlorine could be smelled at the edge of the pond at various times while the gas flow was varying from 5,000 to 40,000 cc/min; the rise path was 15 feet. Whether the undissolved chlorine was 20 or 80 percent of initial flow is probably unimportant.

Therefore, the role of water in mitigating the toxicity problem of a chlorine leak is limited to insignificantly small leaks. Or, if one assumes that small leaks ultimately become big leaks because of corrosion, the rise path through water gives one a few hours to contemplate the situation. It seems inconceivable that a large tank could empty itself of tons of chlorine without atmospheric dispersion.

As for the underwater release of liquid chlorine, we have nothing to offer beyond the results of tests #4 and #5. There was some obvious chlorine loss, perhaps 90 percent, when one gallon of liquid was released under 10 feet of water; there was no measurable loss when 5 gallons of liquid was released under 4 feet of water.

In tests #2 and #3, the chlorine released over water was well accounted for at the downwind sampling stations. However, the distances were admittedly too short to prove that solubility would not be a major factor in a large-scale incident.

G. Estimation of Hazard

The scaling laws for blast wave propagation from explosives have been known for many years, and much of our feeling for the hazards of toxic materials are based on simple analogy with explosive hazards. It is the sense of the two following paragraphs that the analogy is not a good one in the case of chlorine.

Suppose that one has a weight of explosive, W, to be shipped in n consignments so that each consignment consists of $\frac{W}{n}$ pounds of explosive. The probability of an accidental detonation, P, is proportional to n; the area, A, devastated by one explosion is proportional to $(\frac{W}{n})^{2/3}$ because of the three-dimensional expansion of the blast wave. Therefore,

$$P \propto n$$

$$A \propto \left(\frac{W}{n}\right)^{2/3}$$

$$\text{Hazard} \propto P \cdot A \propto n \left(\frac{W}{n}\right)^{2/3} = n^{1/3} W^{2/3}$$

So the total hazard is clearly reduced by reducing n, that is, by shipping in larger consignments.

If a toxic gas expanded in a cloud with spherical symmetry, the same conclusion as to hazard would be valid. But with consideration for layering and wind direction, we obtain a much different result. Consider the chlorine flash-vaporized on rupture of a tank: Q in equation (1) is proportional to $\frac{W}{n}$ and the maximum distance, x, at which one finds some critical dosage is given by (assuming stable atmosphere)

$$x^{1.4} \propto \frac{W}{n}$$

The area so covered is nearly proportional to $x\ \sigma_y$ or to $x^{1.7}$. Therefore, $P \cdot A = n\ (\frac{W}{n})^{\frac{1.7}{1.4}} = n\ (\frac{W}{n})^{1.2} = \frac{W^{1.2}}{n^{0.2}}$. Quite clearly, the total hazard is reduced by increasing the number of consignments, that is, by staying with small individual shipments.

VII. CONCLUSIONS

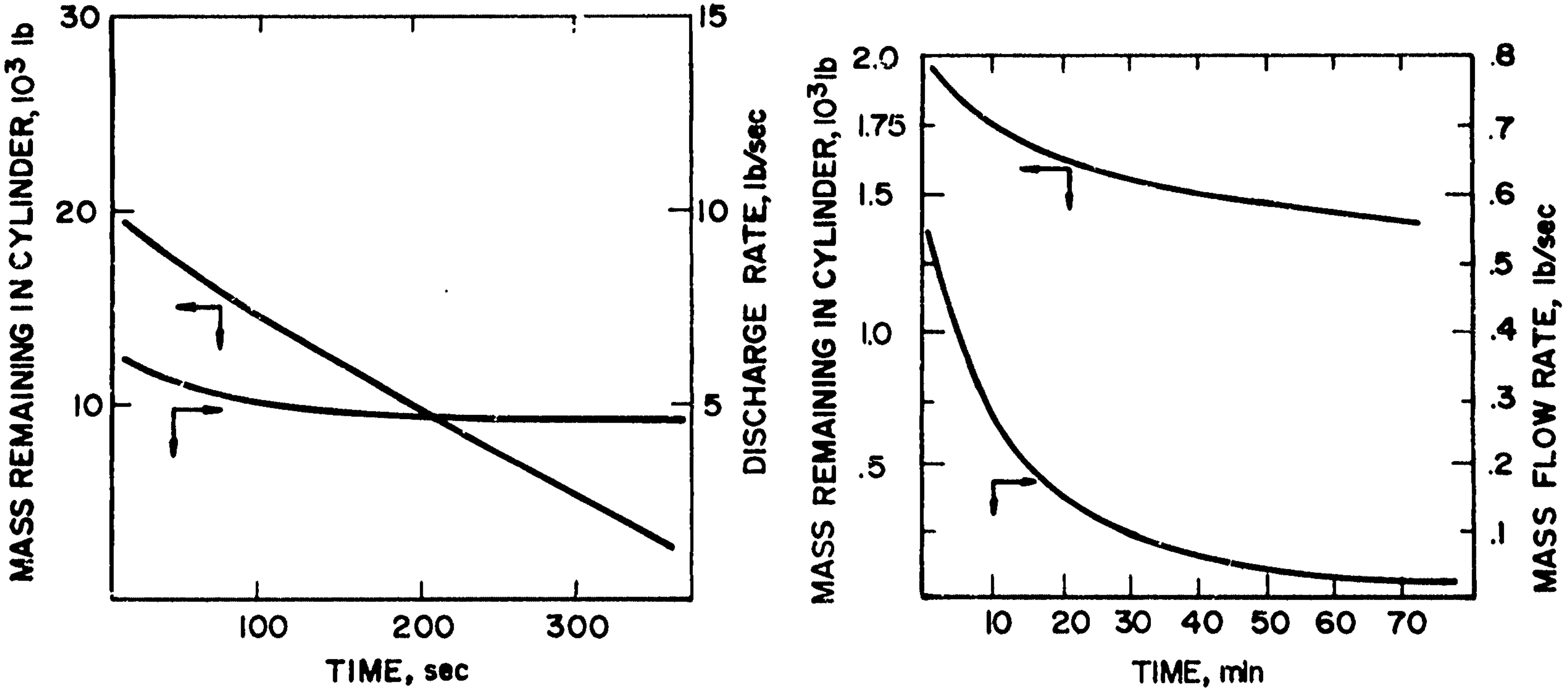
Experiments that were directed at specific questions concerning chlorine release in water have given these results:

1. The rate of vaporization of chlorine is very fast; no evidence was found of a rate-limiting heat transfer across a gas film.

2. Contact with water removes a significant fraction of the chlorine in slow leakage or in small spills; it could hardly be a factor in catastrophic accidents.

3. The leak rate of gaseous chlorine through a hole in ASTM A-516 Grade 70 steel is markedly accelerated by corrosion.

4. Toxic cloud concentrations downwind of a chlorine release are predictable by existing air pollution equations if one makes appropriate correction for heavy gas layering.



(a) (b)

PcN-70200

Figure 1a. - Release rates of (a) liquid and (b) gaseous chlorine through an 0.34-inch orifice from a one-ton cylinder at an initial [illegible]perature of 130° F.

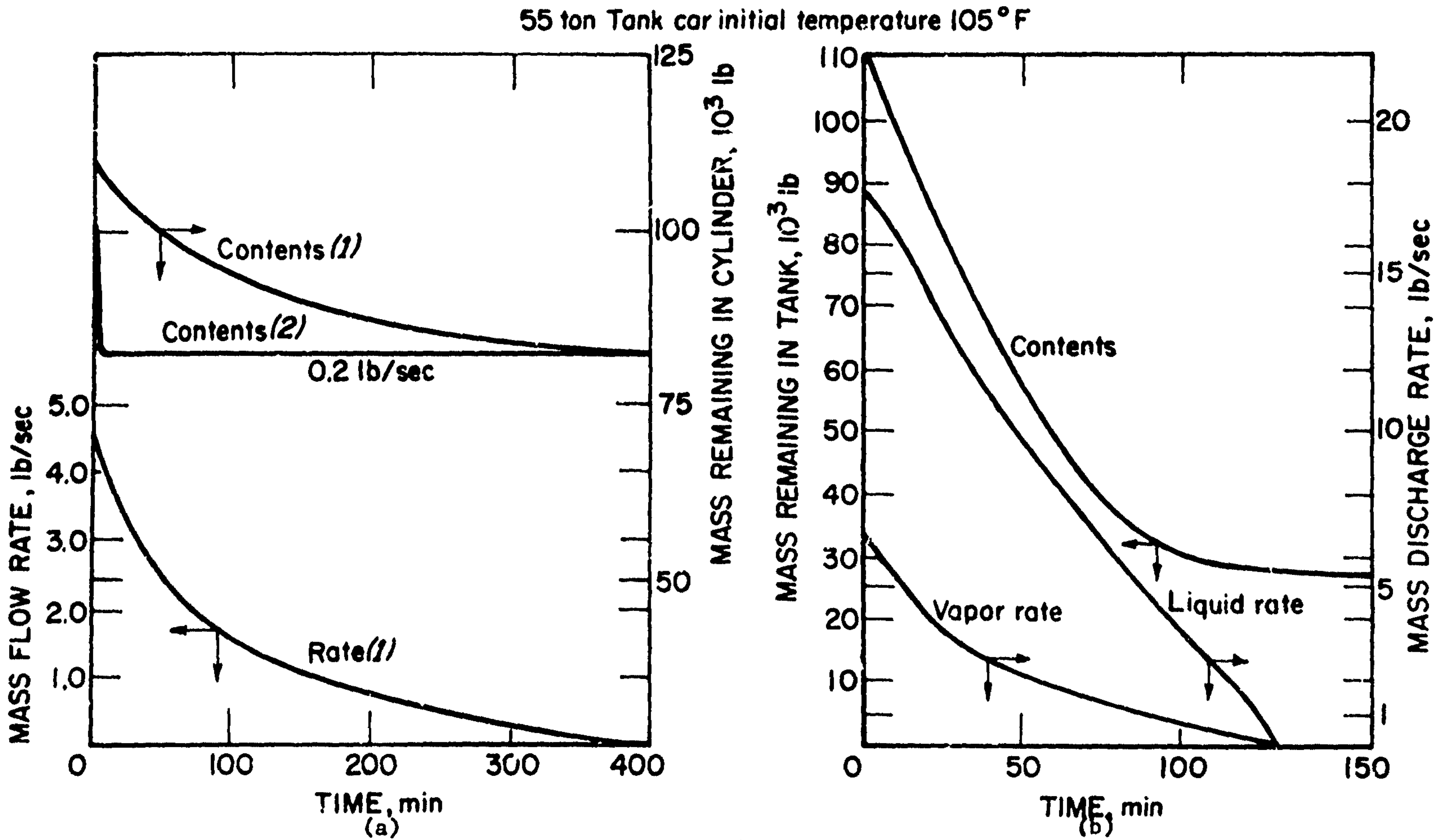
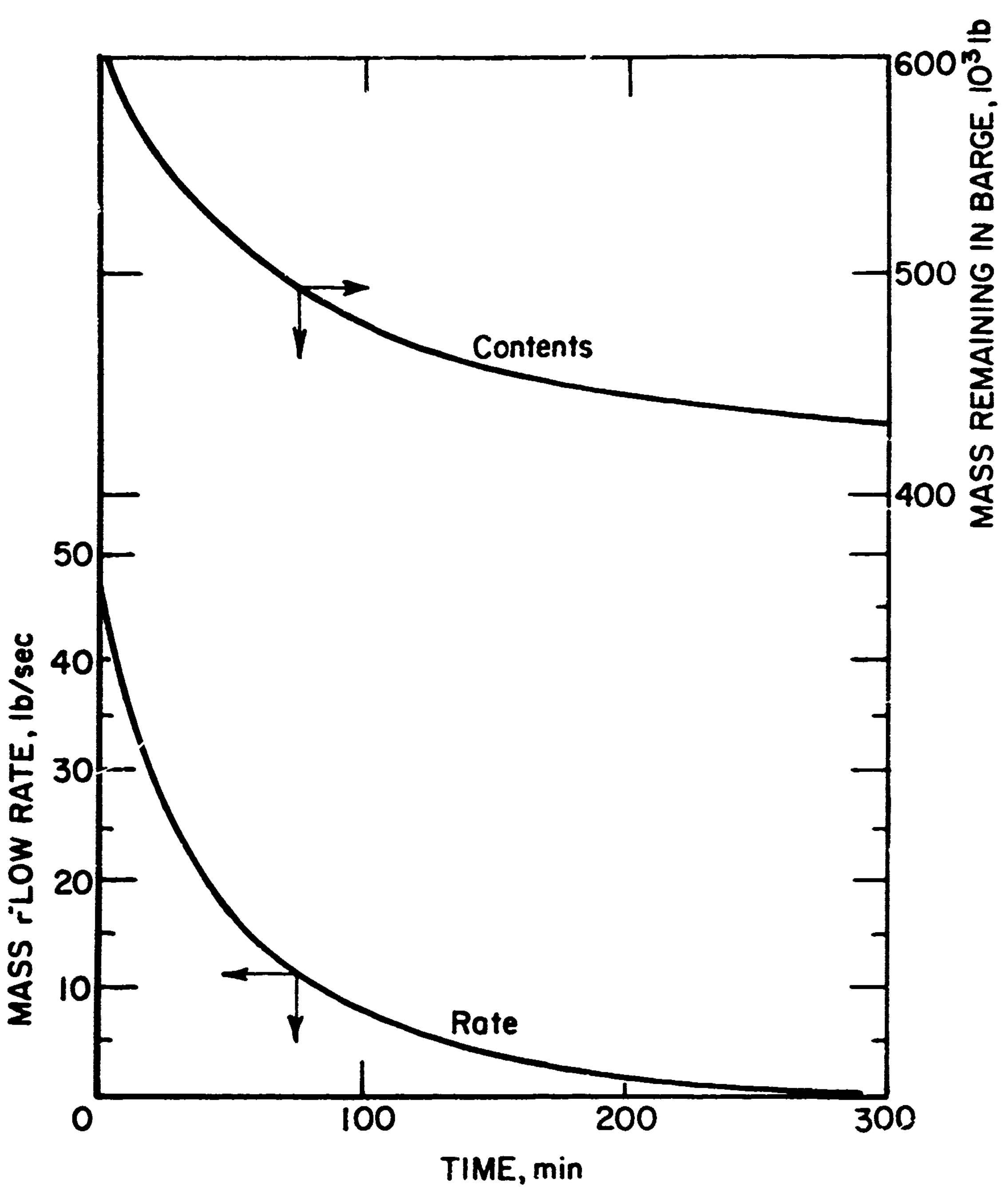


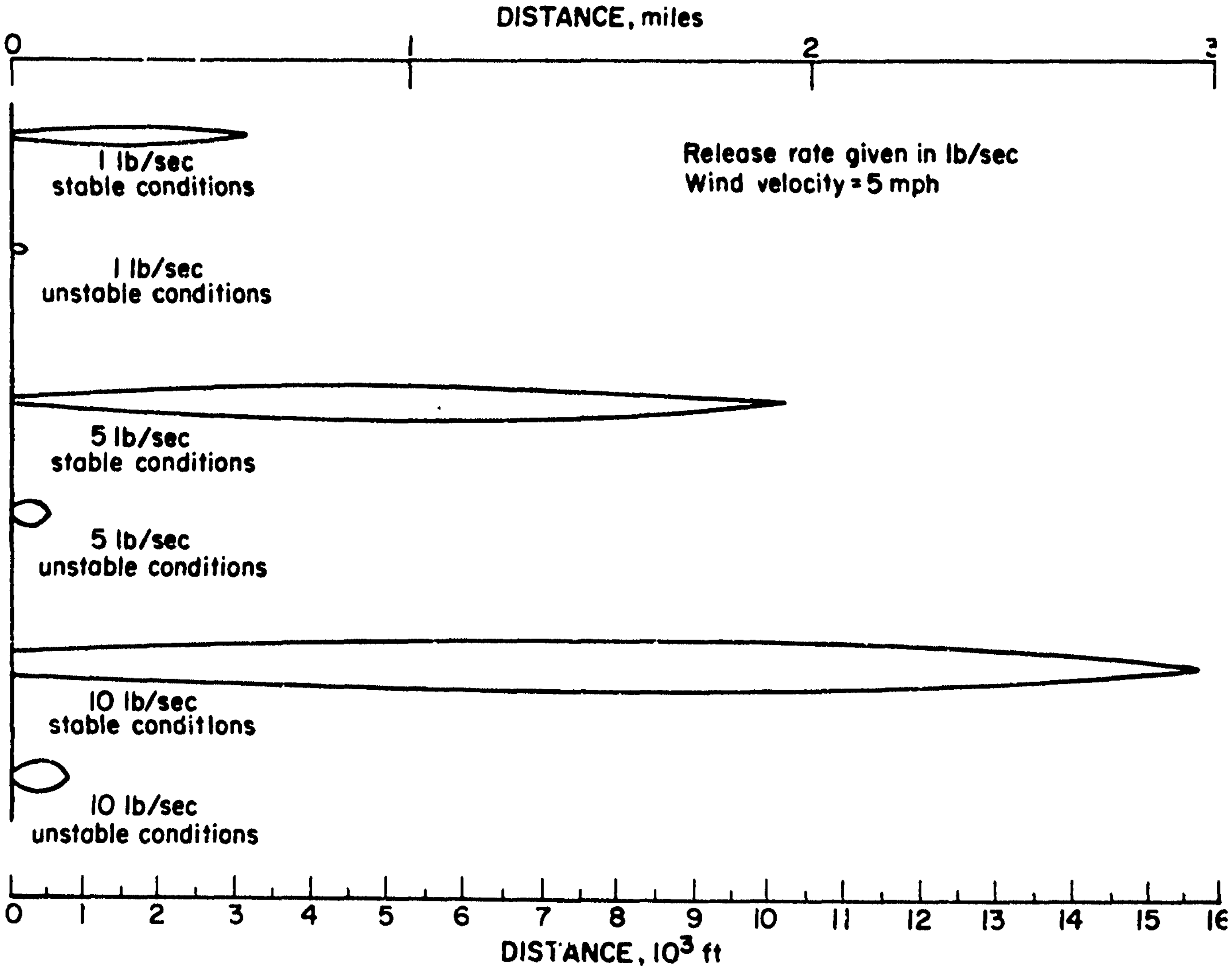
Figure 1b. - Release rates of (a) vapor discharge through (1) a 1-1/8-inch safety valve, and (2) an 18-inch man hole; (b) simultaneous vapor and liquid discharge through two 0.5-inch diameter liquid valves, two 0.5-inch diameter vapor valves, and a 1-1/8-inch diameter safety vapor valve.

P64-70202



PGH-70206

Figure 1c. - Vapor discharge from a 300-ton tank through a 4-inch diameter safety valve with an initial temperature of 150° F.



PGH-70196

Figure 2. - Ground level dispersion of chlorine.

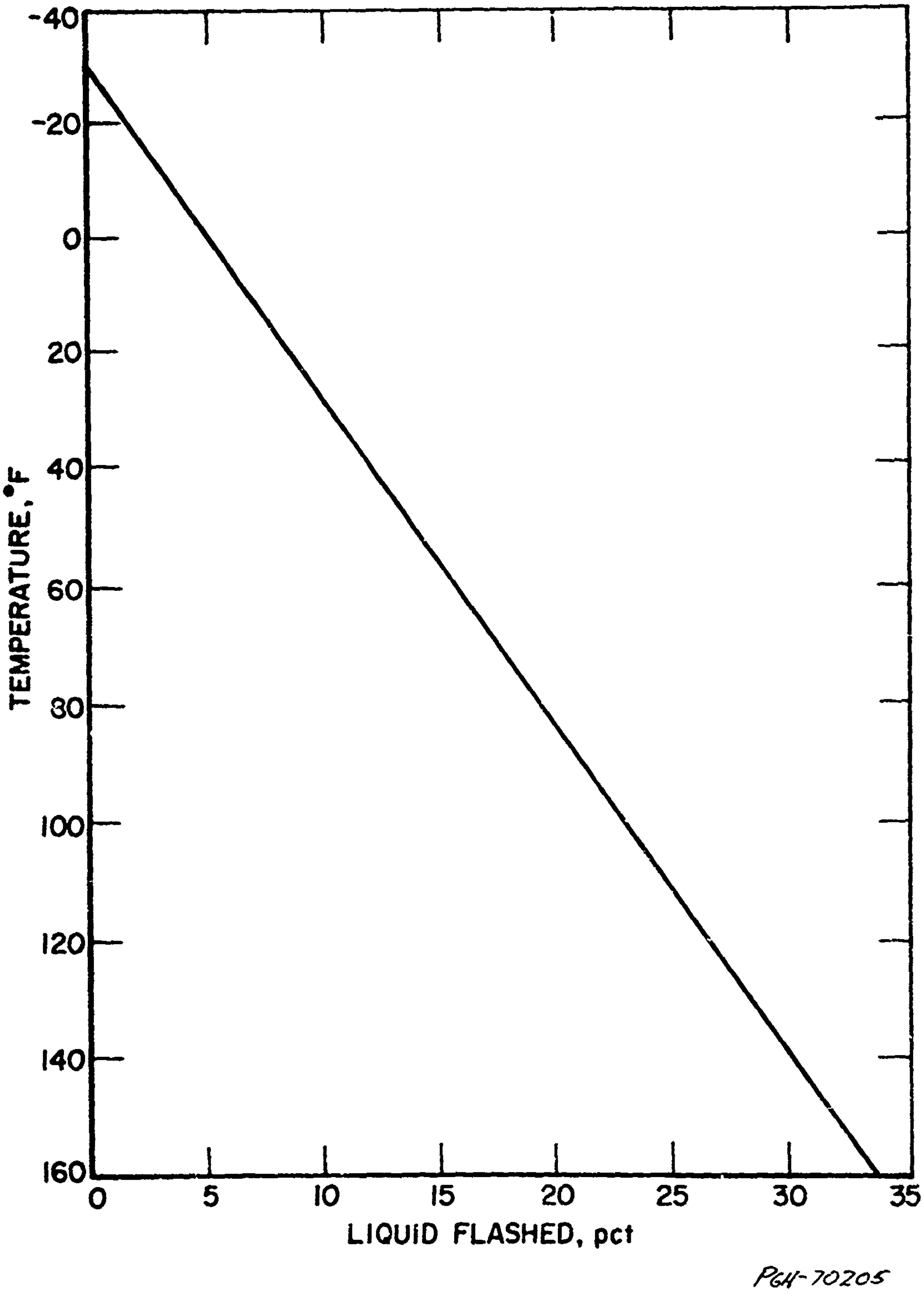
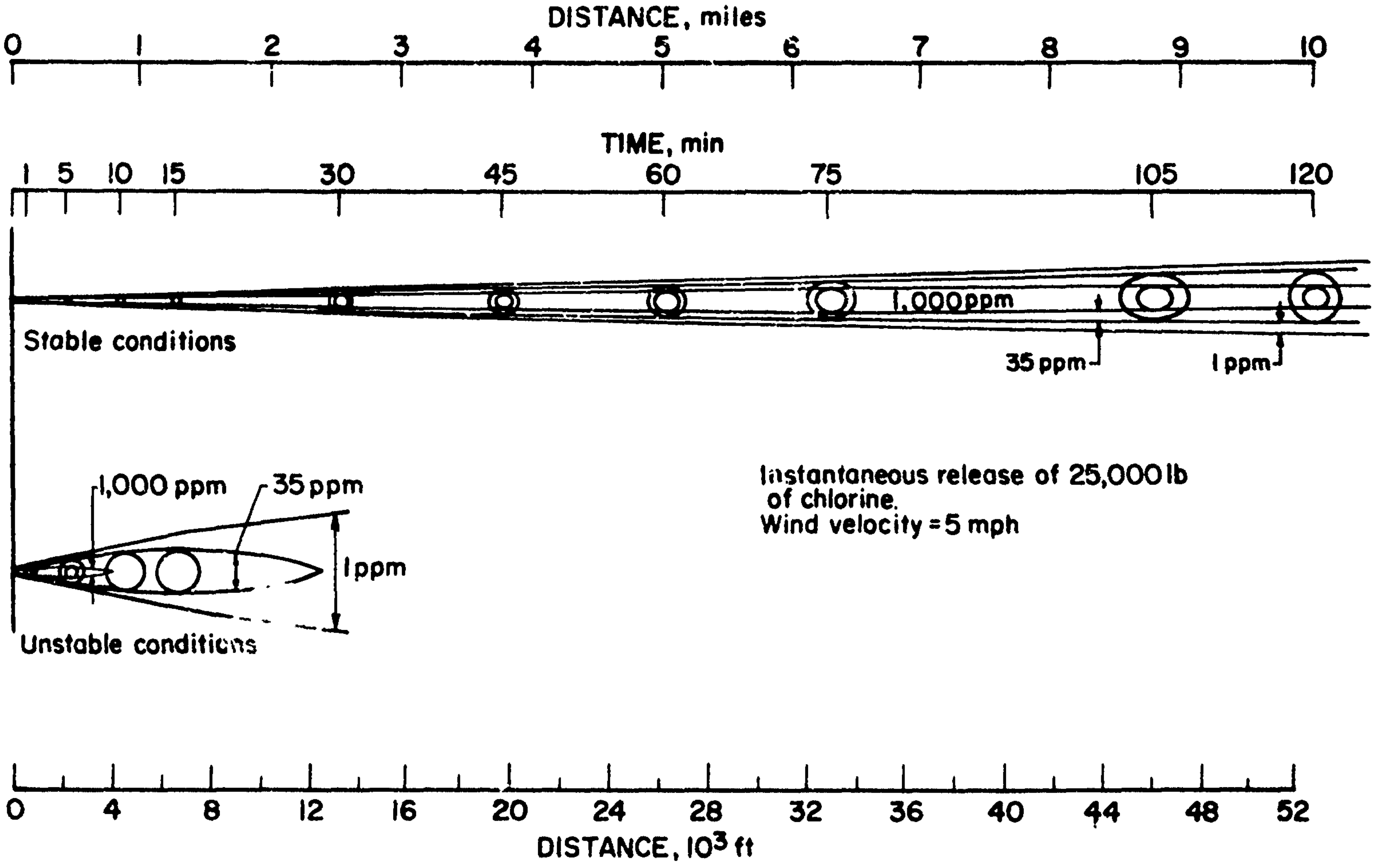
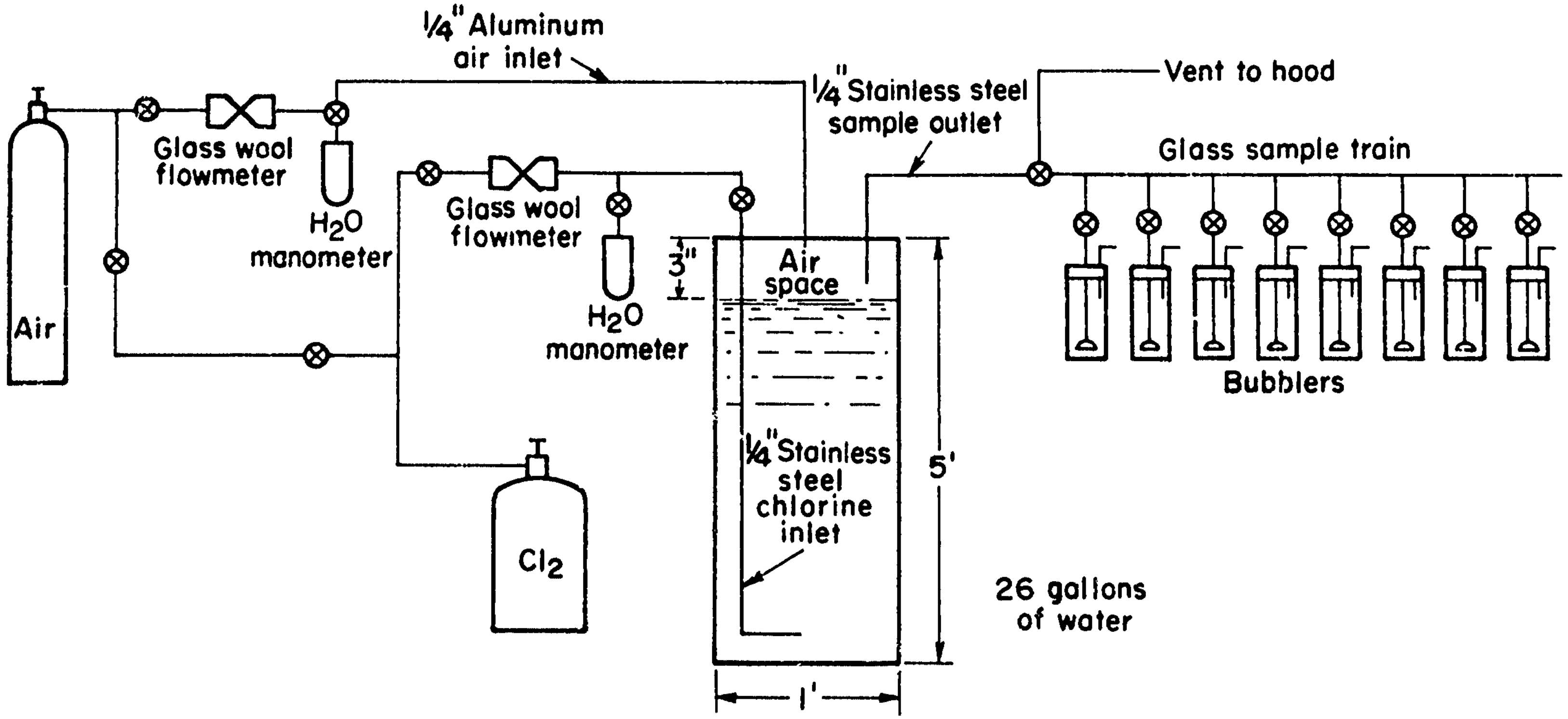


Figure 3. - Percentage of liquid flashed vs initial container temperature.



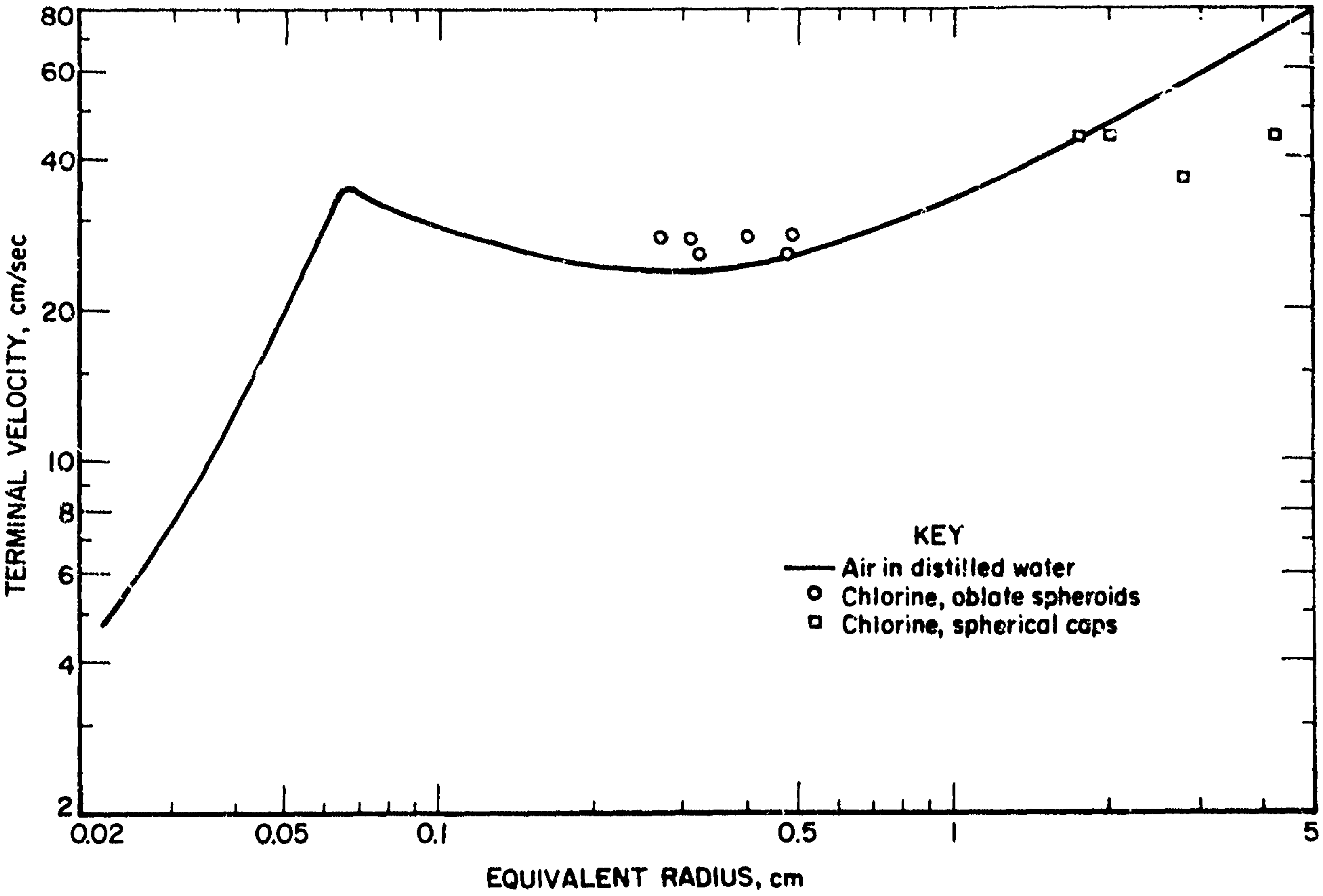
PGH-70197

Figure 4. - Downwind dispersal of an instantaneous release of gaseous chlorine.



PGH-70204

Figure 5. - Schematic diagram of laboratory apparatus.



PGH-70207

Figure 6. - Terminal velocity of gas bubbles in water as a function of bubble size.

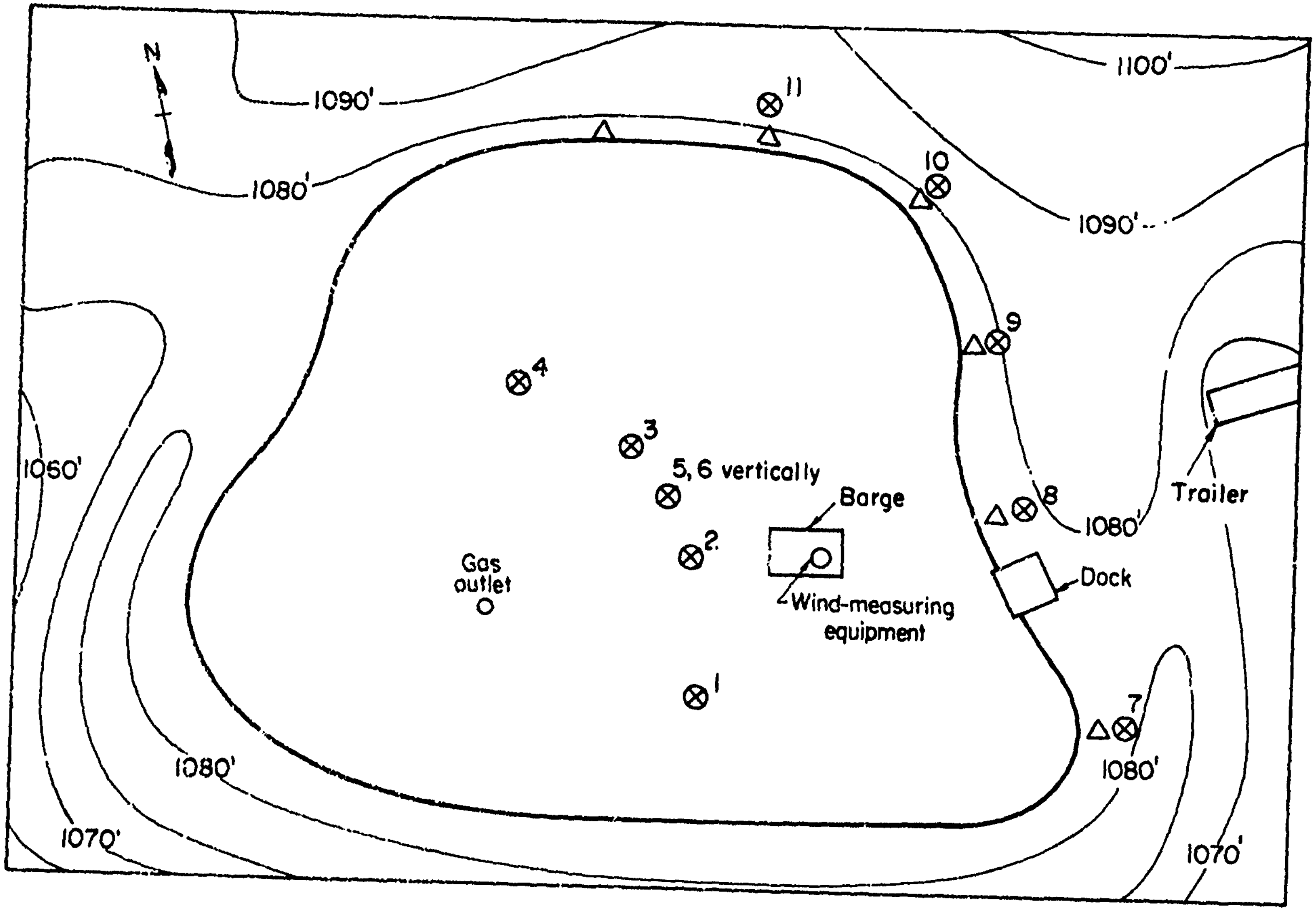
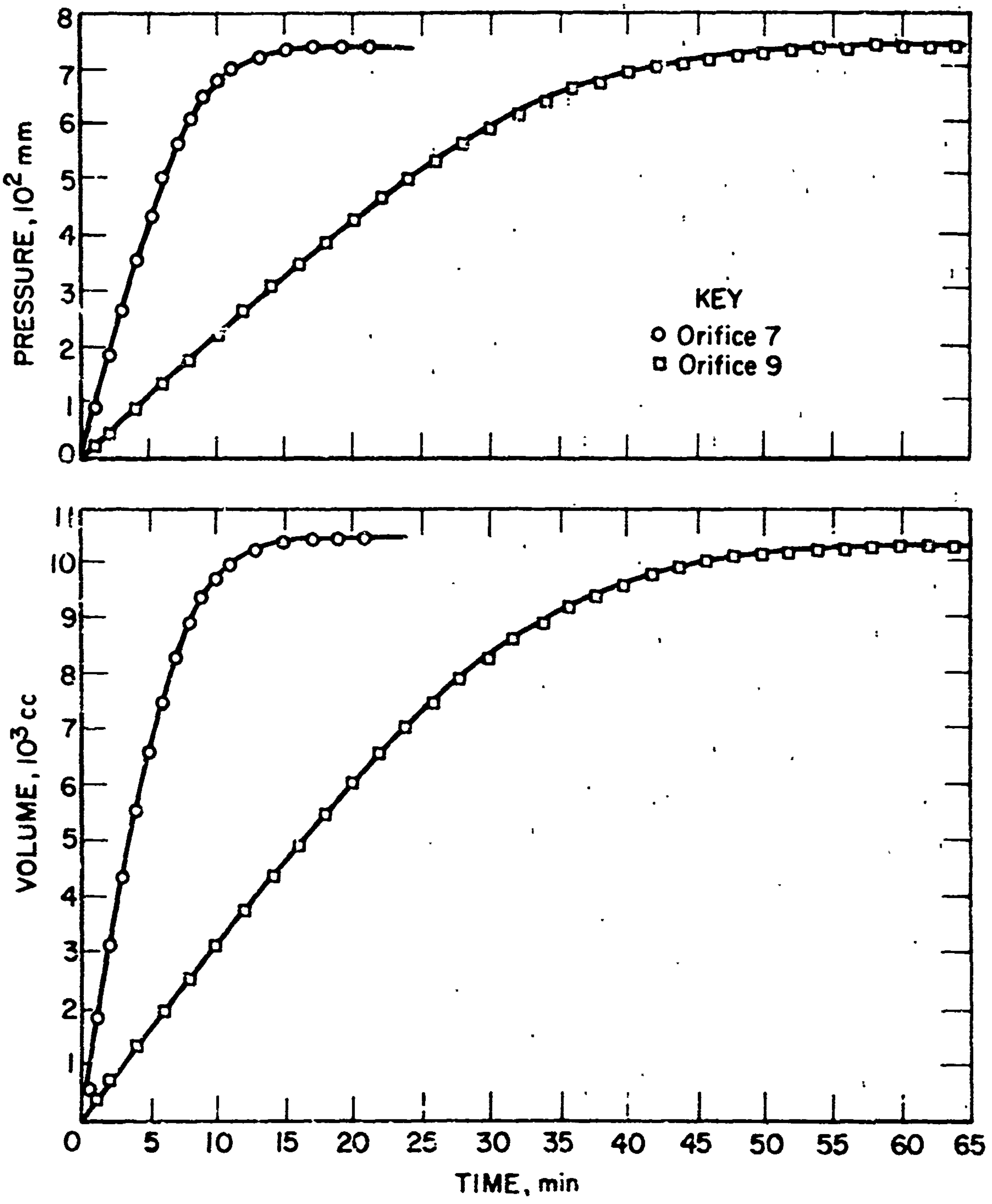


Figure 7. - Arrangement of test site for large-scale experiments.

PGH-70189



PGH-70203

Figure 8. - Typical pressure and volume rates of sample into evacuated bottles through hypodermic-type needles.

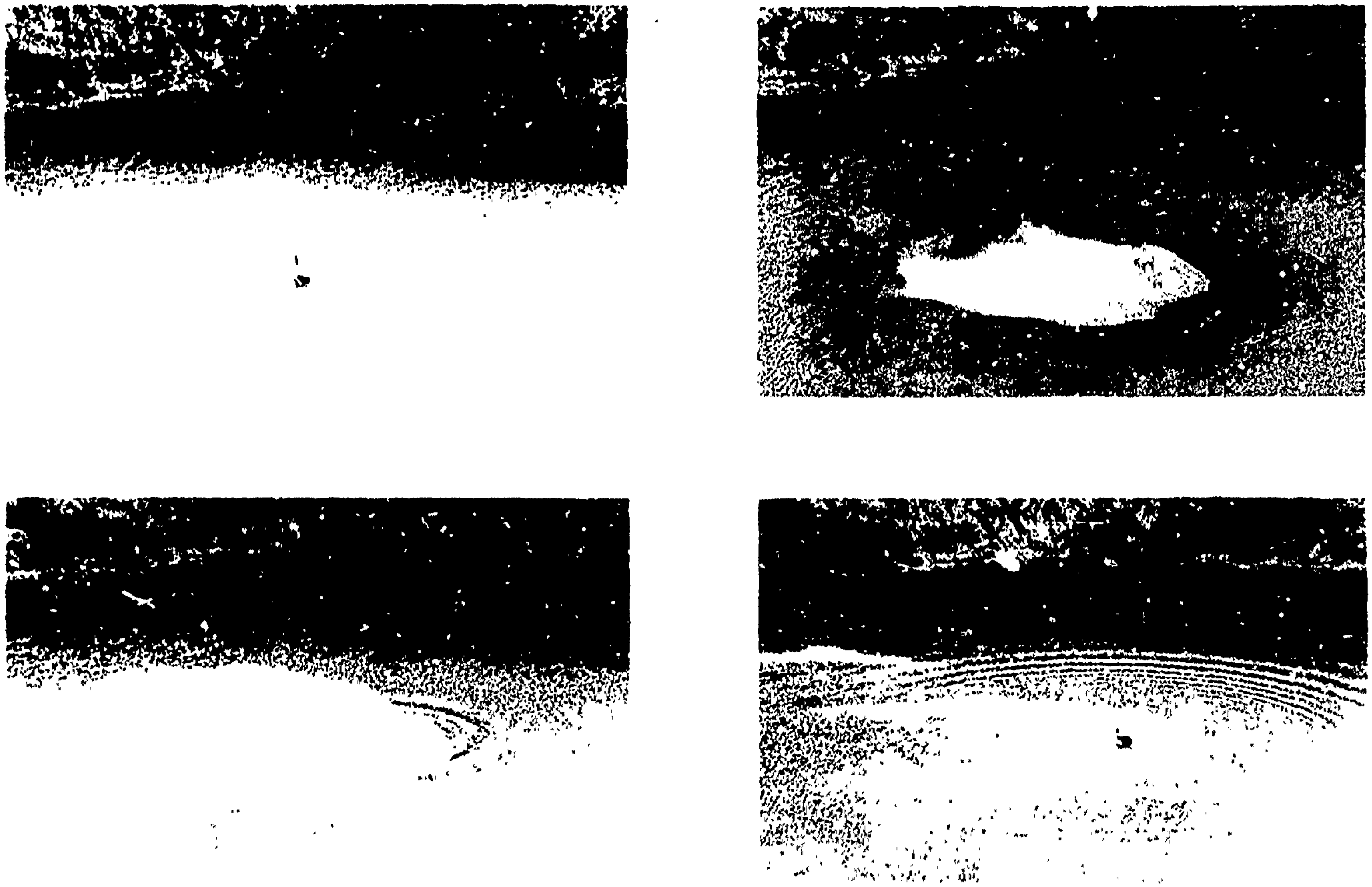


Figure 9. - Spillage of 10 gallons of liquid chlorine onto water. Time between pictures is approximately 7 seconds.

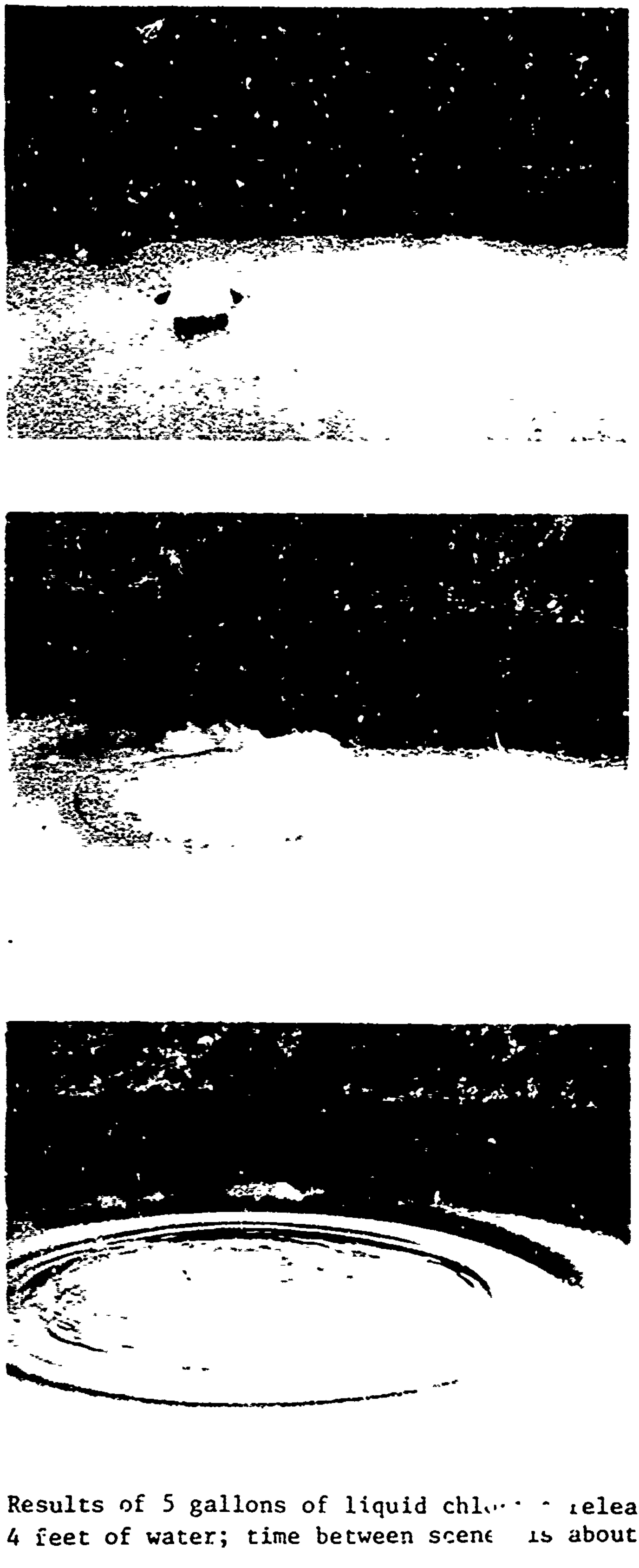


Figure 10. - Results of 5 gallons of liquid chlorine released under 4 feet of water; time between scenes is about 10 seconds.

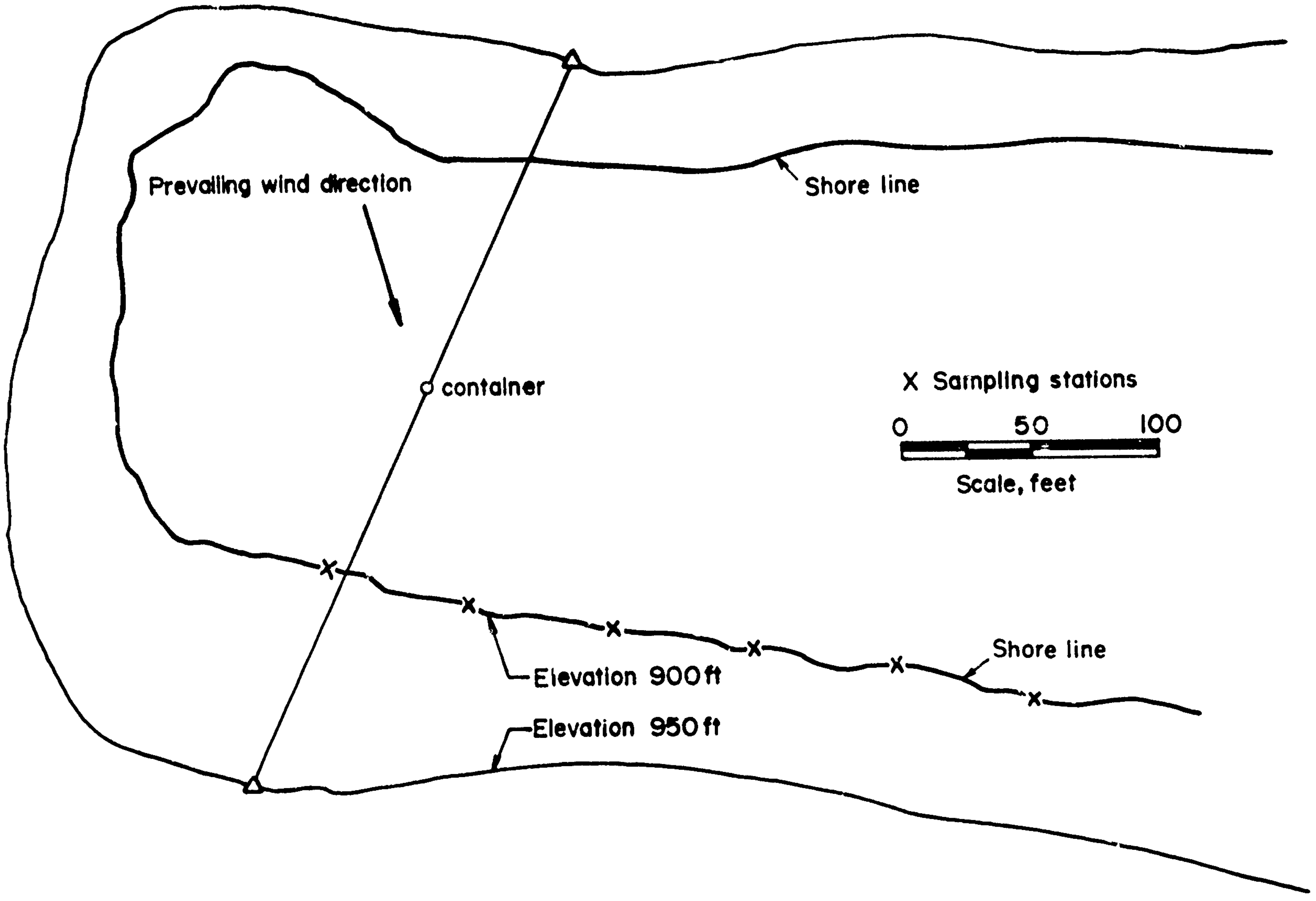
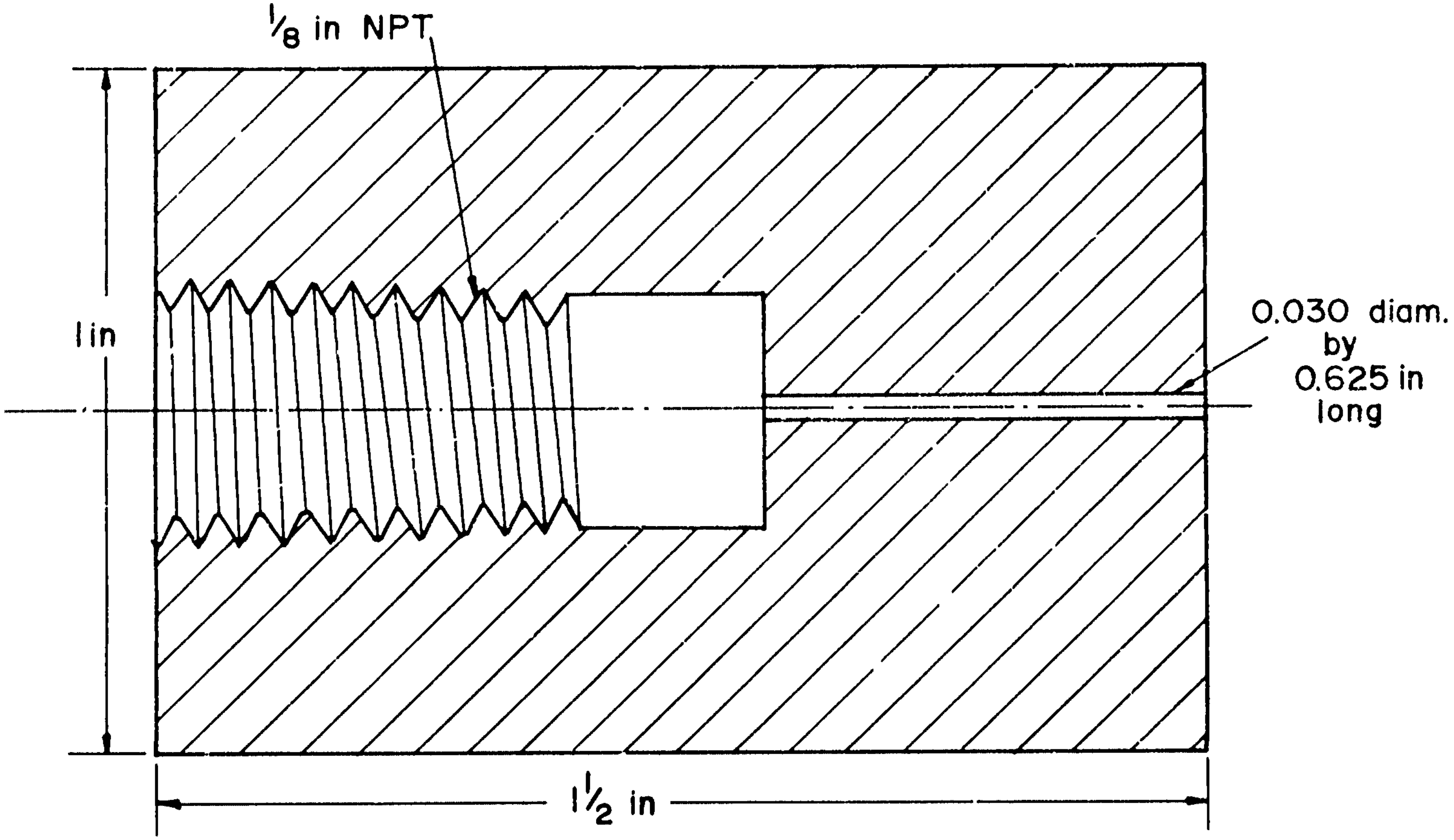


Figure 11. - Schematic of lake showing spill apparatus and sampling stations.

PGH-70199



PGN-70198

Figure 12. - Schematic of ASTM A516 Grade 70 steel block used in corrosion tests.

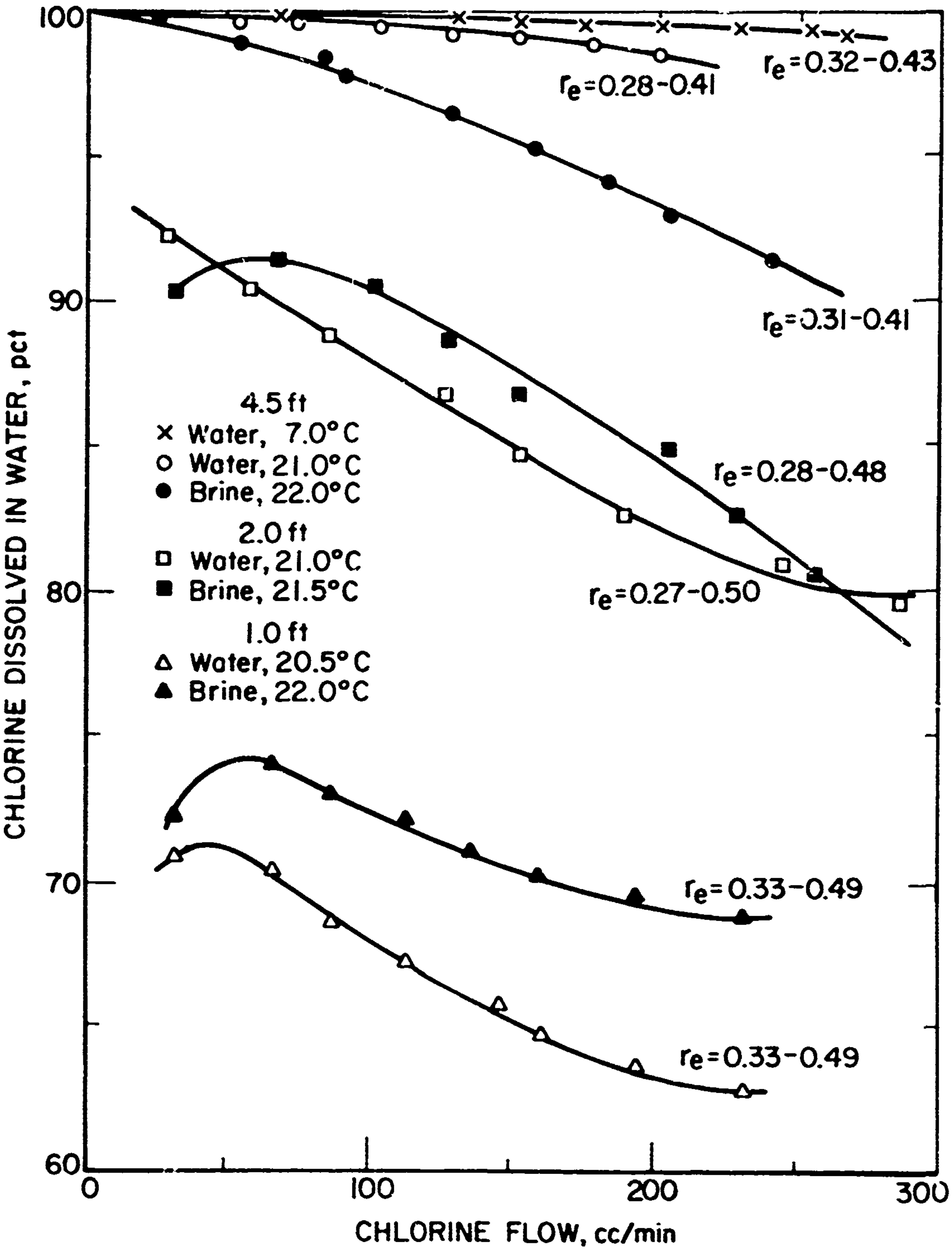
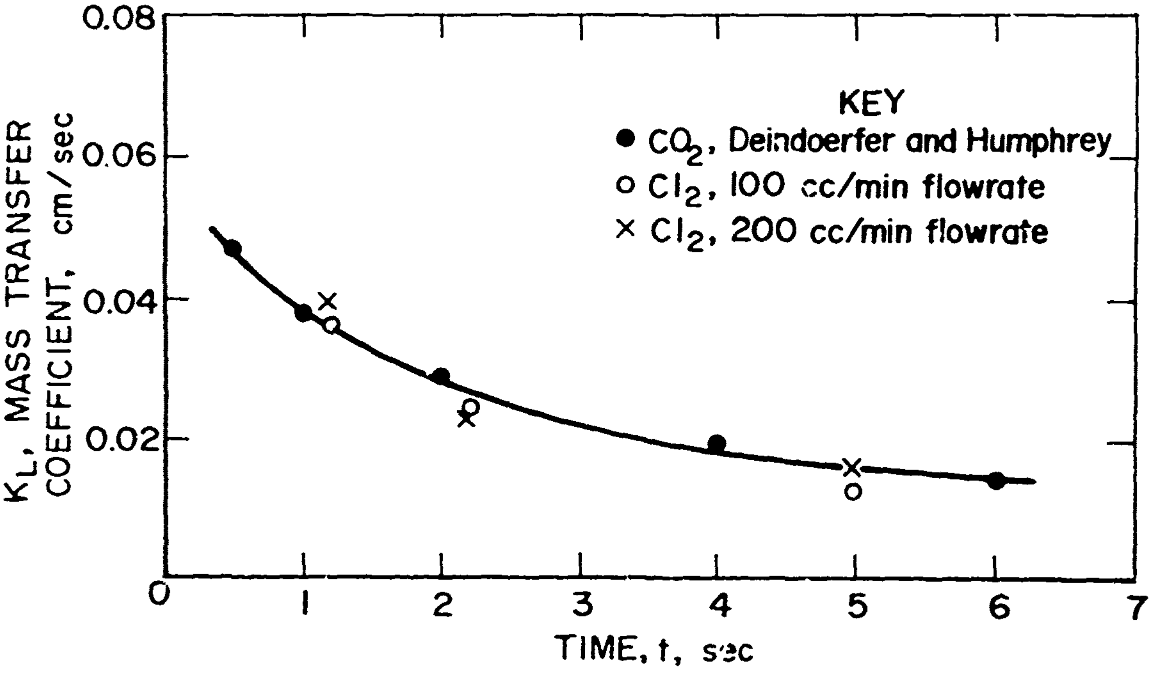


Figure 13. - Percent chlorine dissolved in water at room temperature, 7° C, and in brine for underwater depths of 4.5, 2.0, and 1.0 foot.



PGH-70193

Figure 14. - Instantaneous transfer coefficients as a function of time or bubble age.

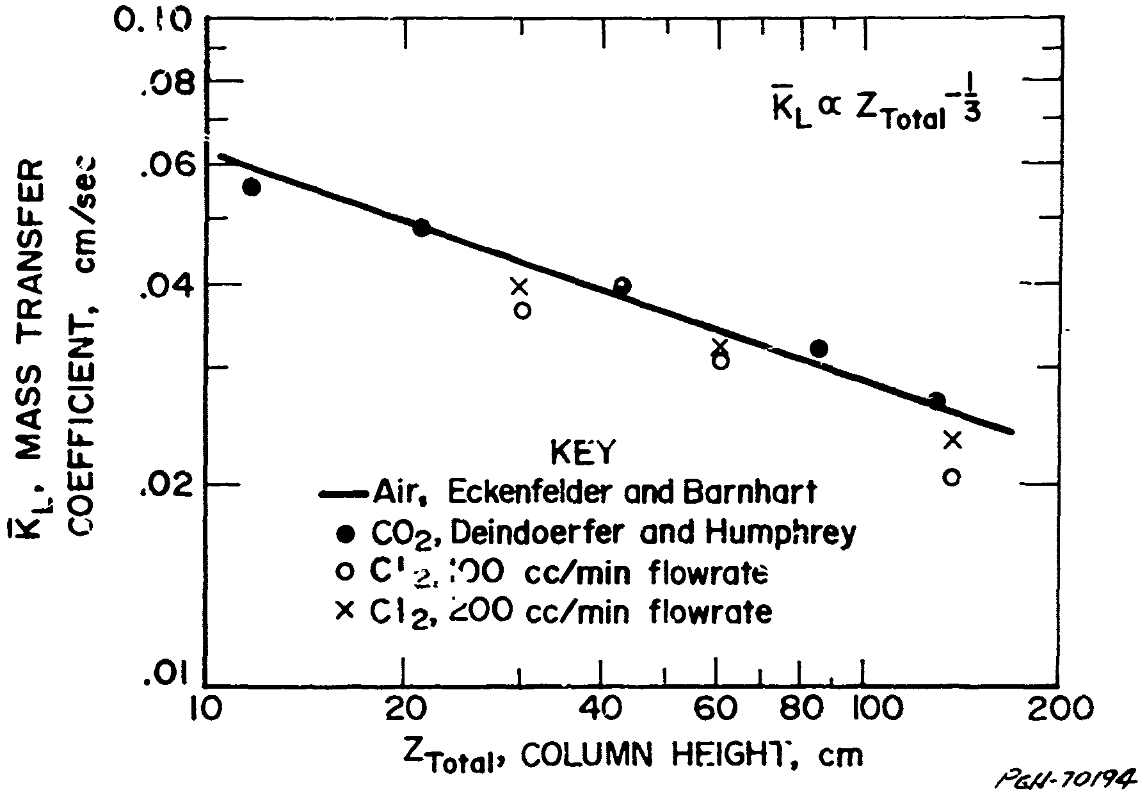
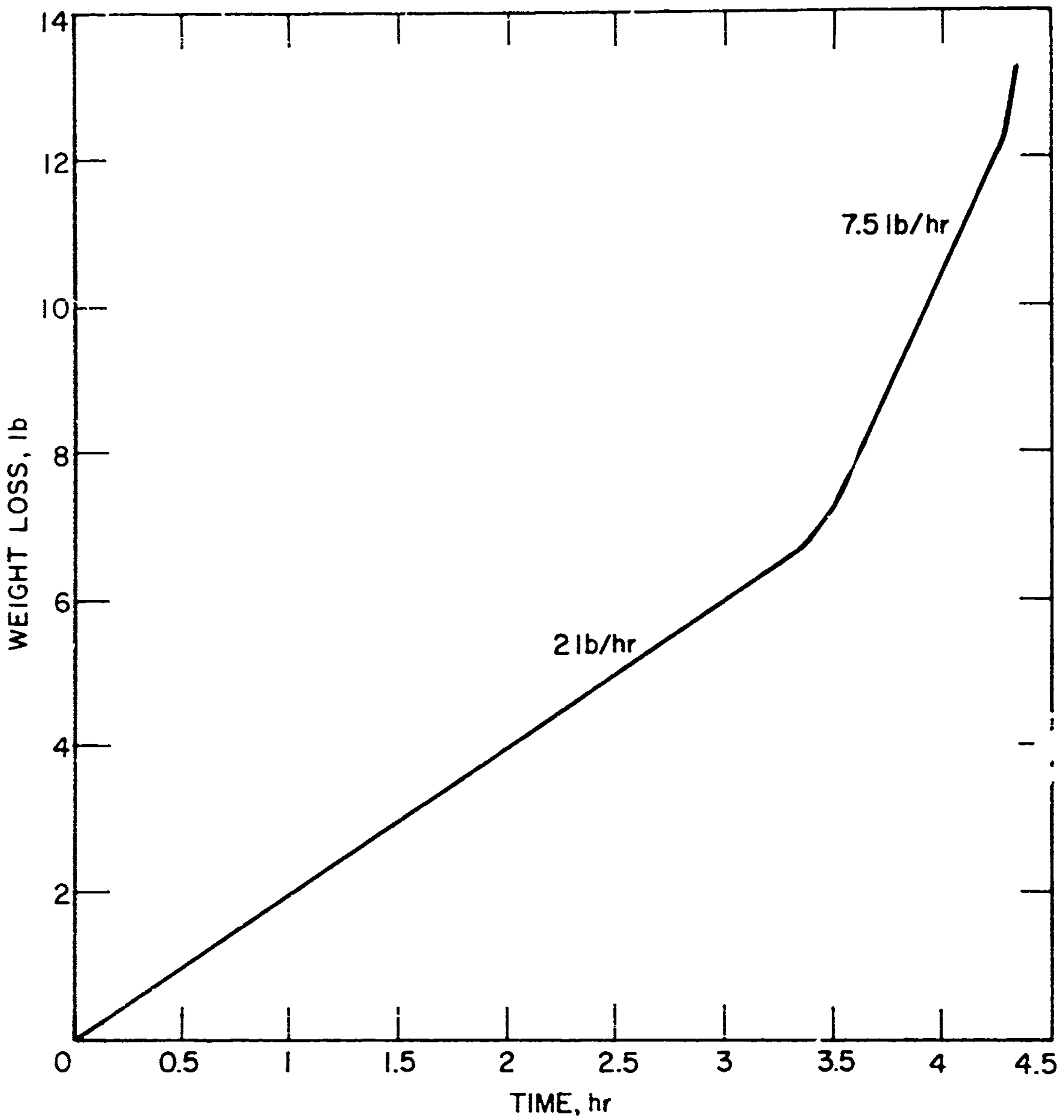


Figure 15. - Comparison of integrated mass transfer coefficients for various gases.



PGH-70195

Figure 16. - Effect of gaseous chlorine at 10 psig flowing through a 0.030" diameter x 0.625" long hole in ASTM A-516 steel contained in an aqueous environment.

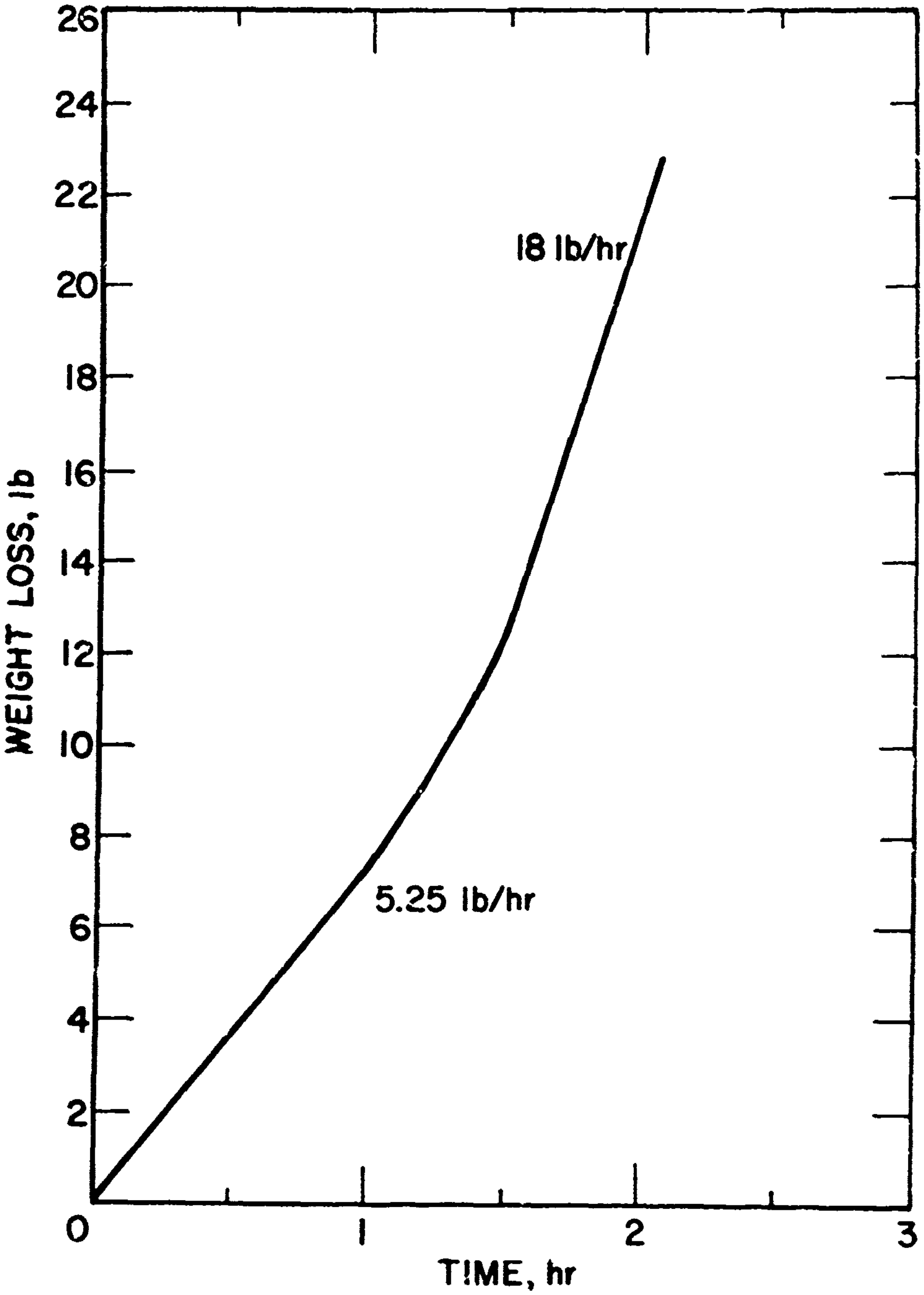


Figure 17. - Effect of gaseous chlorine at 90 psig flowing through a 0.030" diameter x 0.625" long hole in ASTM A-516 steel contained in an aqueous environment.

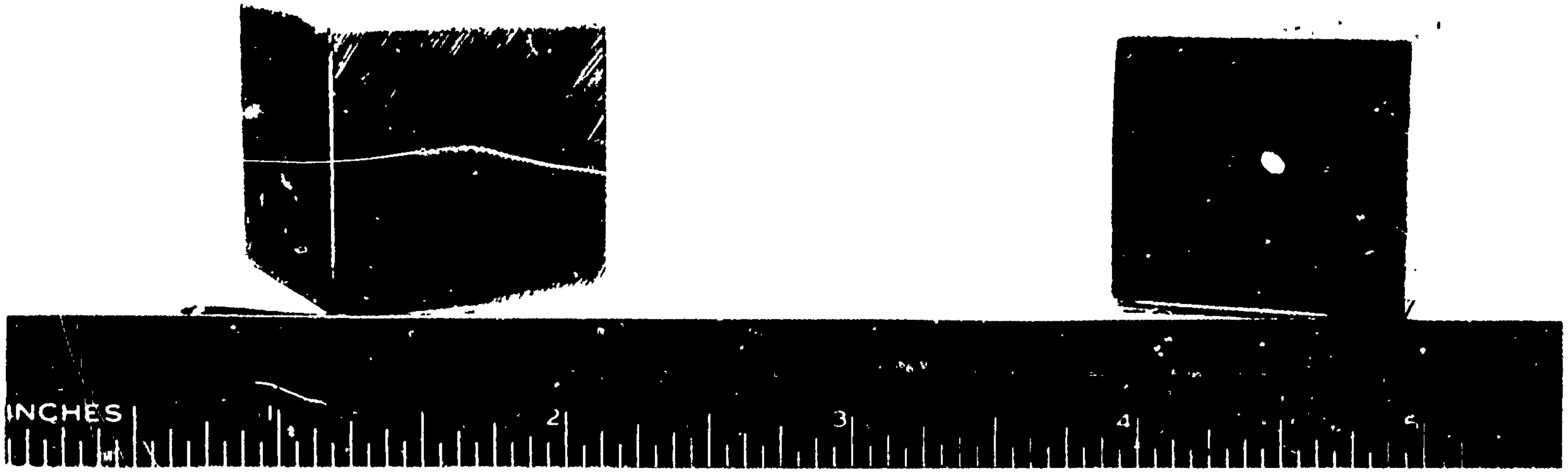
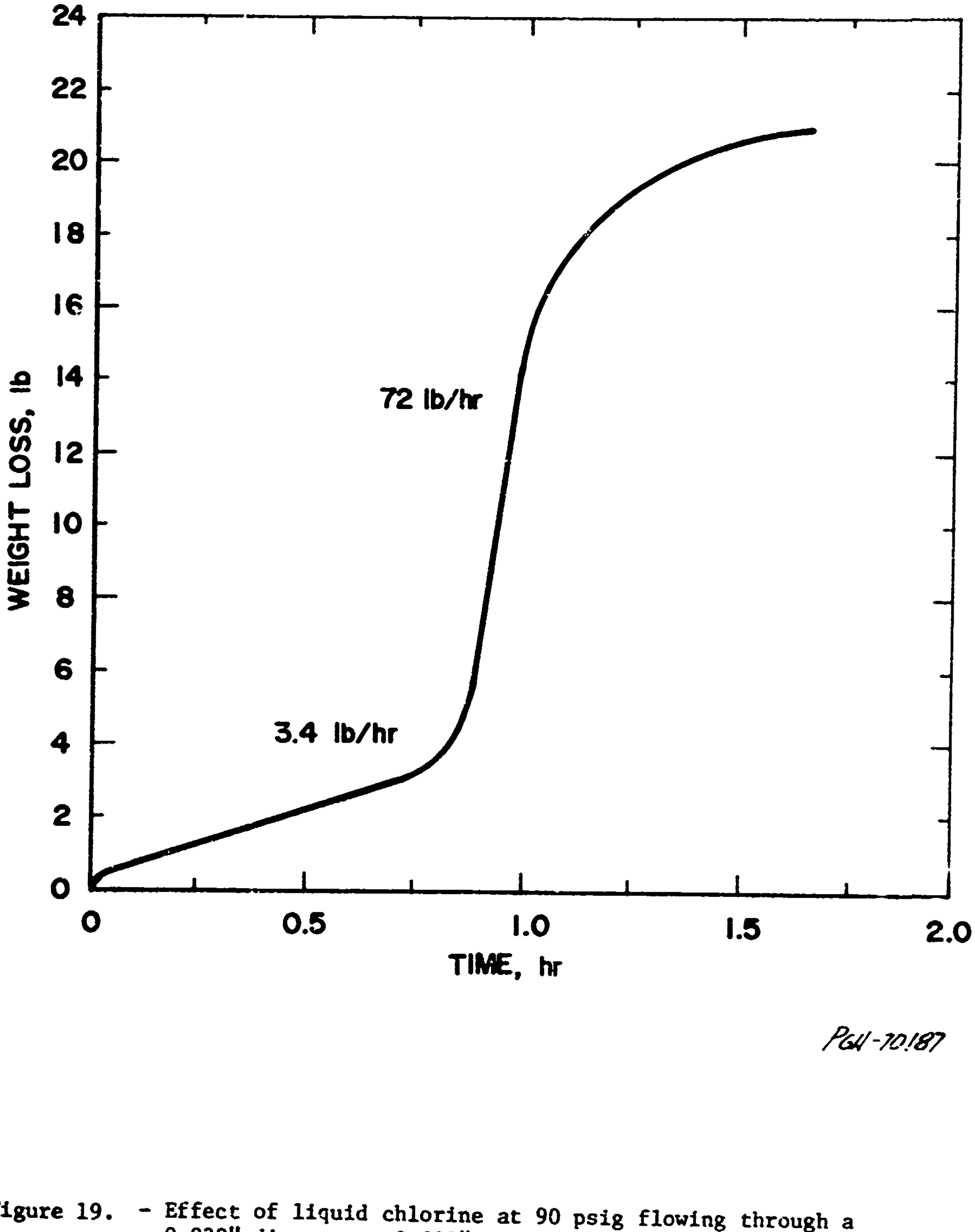
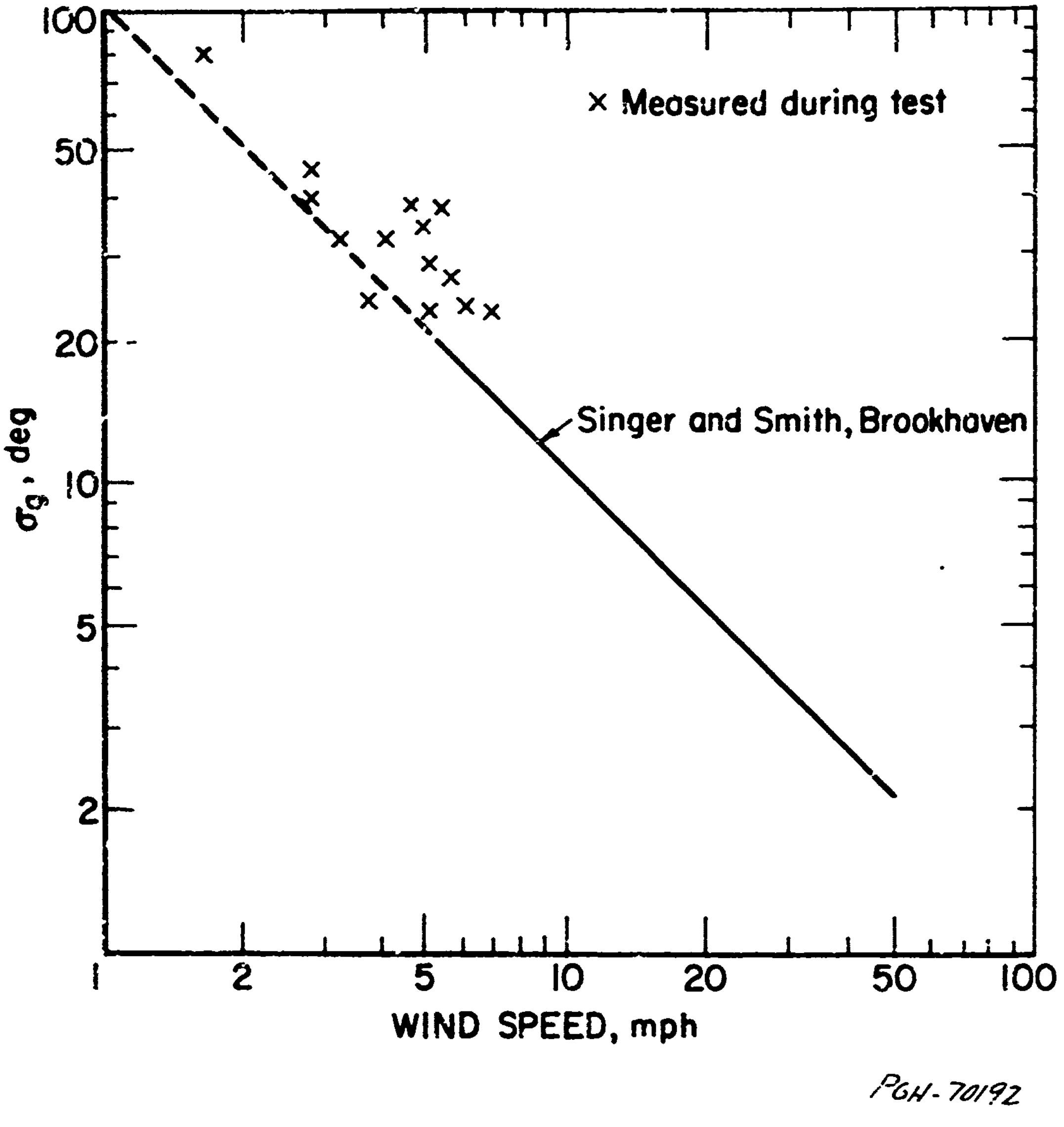


Figure 18. - Block of steel used for corrosion tests (left) before experiment and (right) after gaseous chlorine at 90 psig was flowed for 2 hours.



PGH-70187

Figure 19. - Effect of liquid chlorine at 90 psig flowing through a 0.030" diameter x 0.625" long hole in ASTM A-516 steel contained in an aqueous environment.



PGH-70192

Figure 20. - Wind speed and standard deviation of direction.

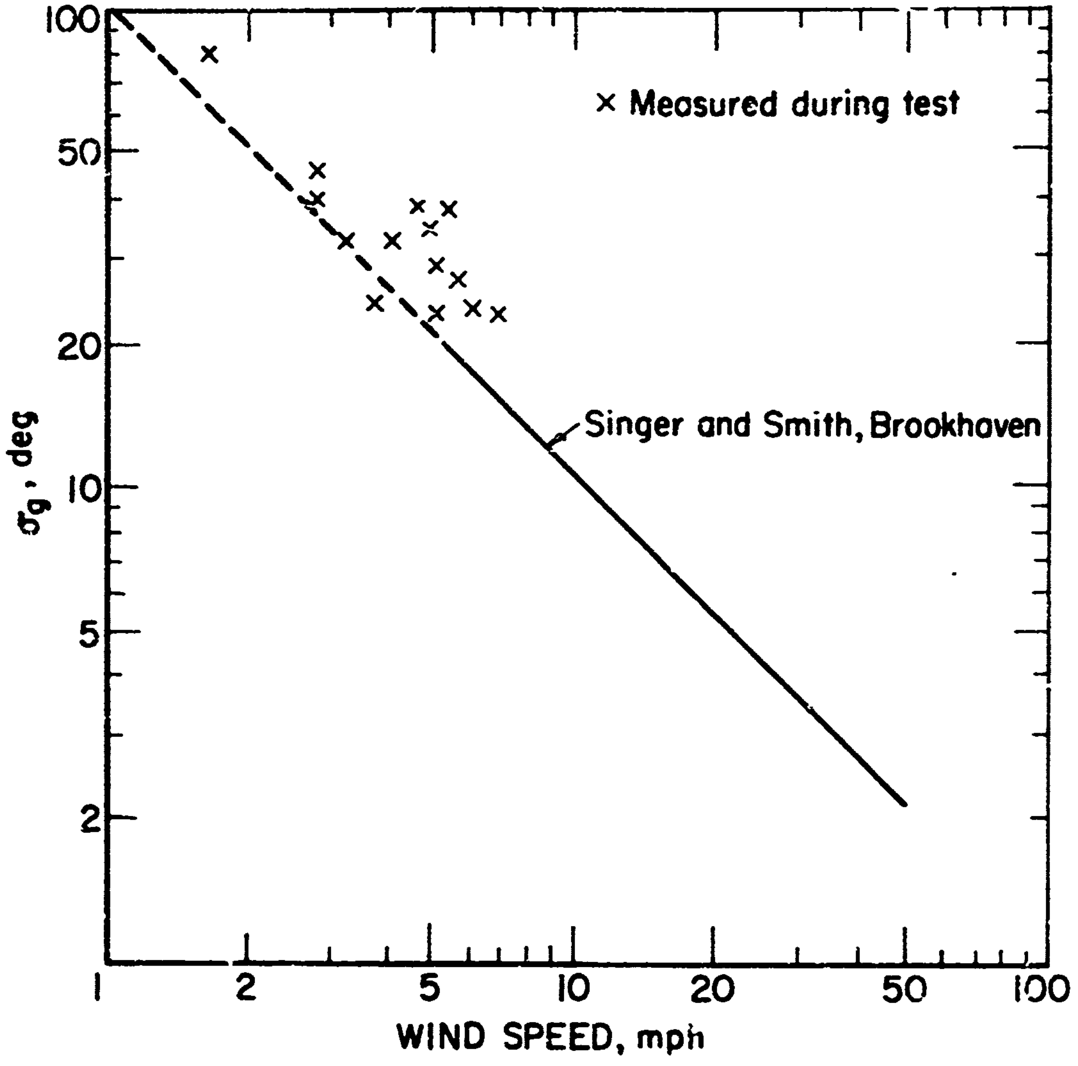


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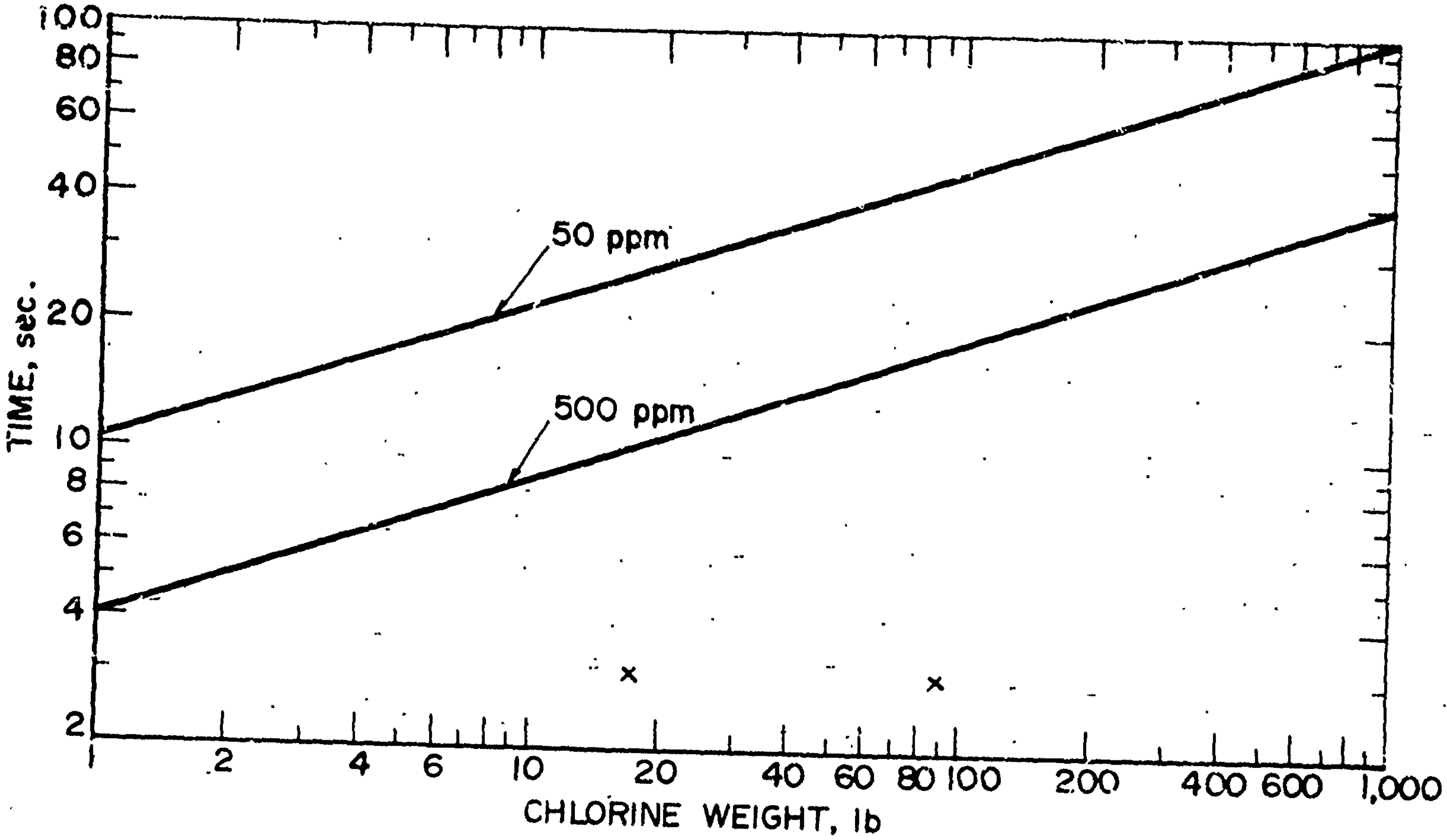
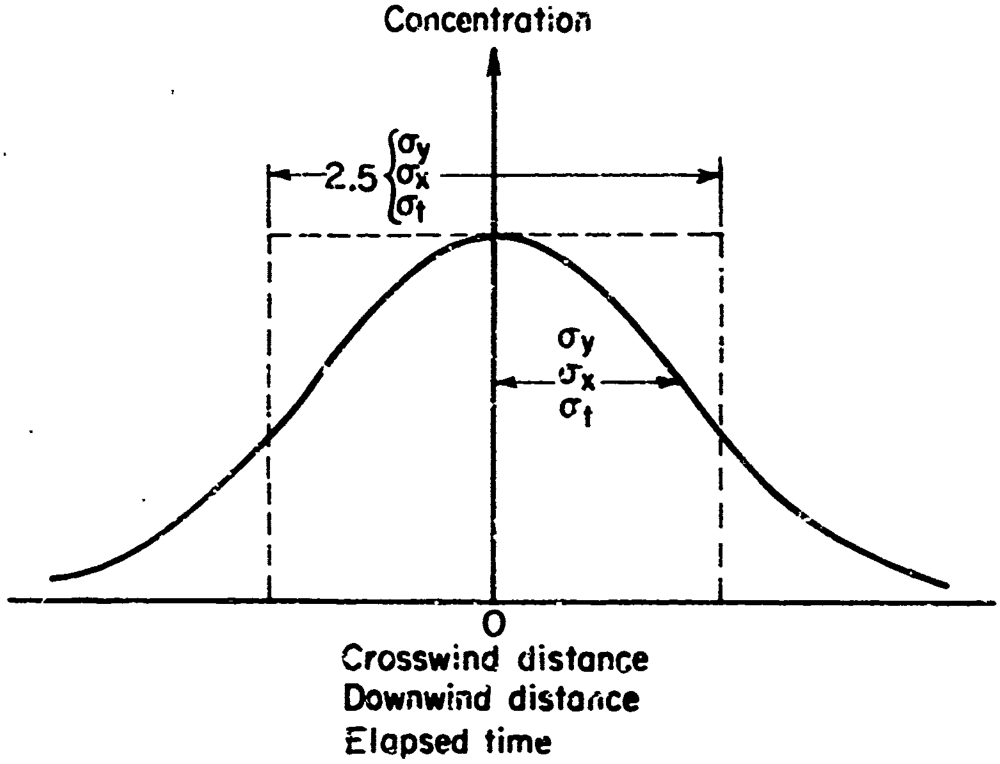
Figure 20. - Wind speed and standard deviation of direction.



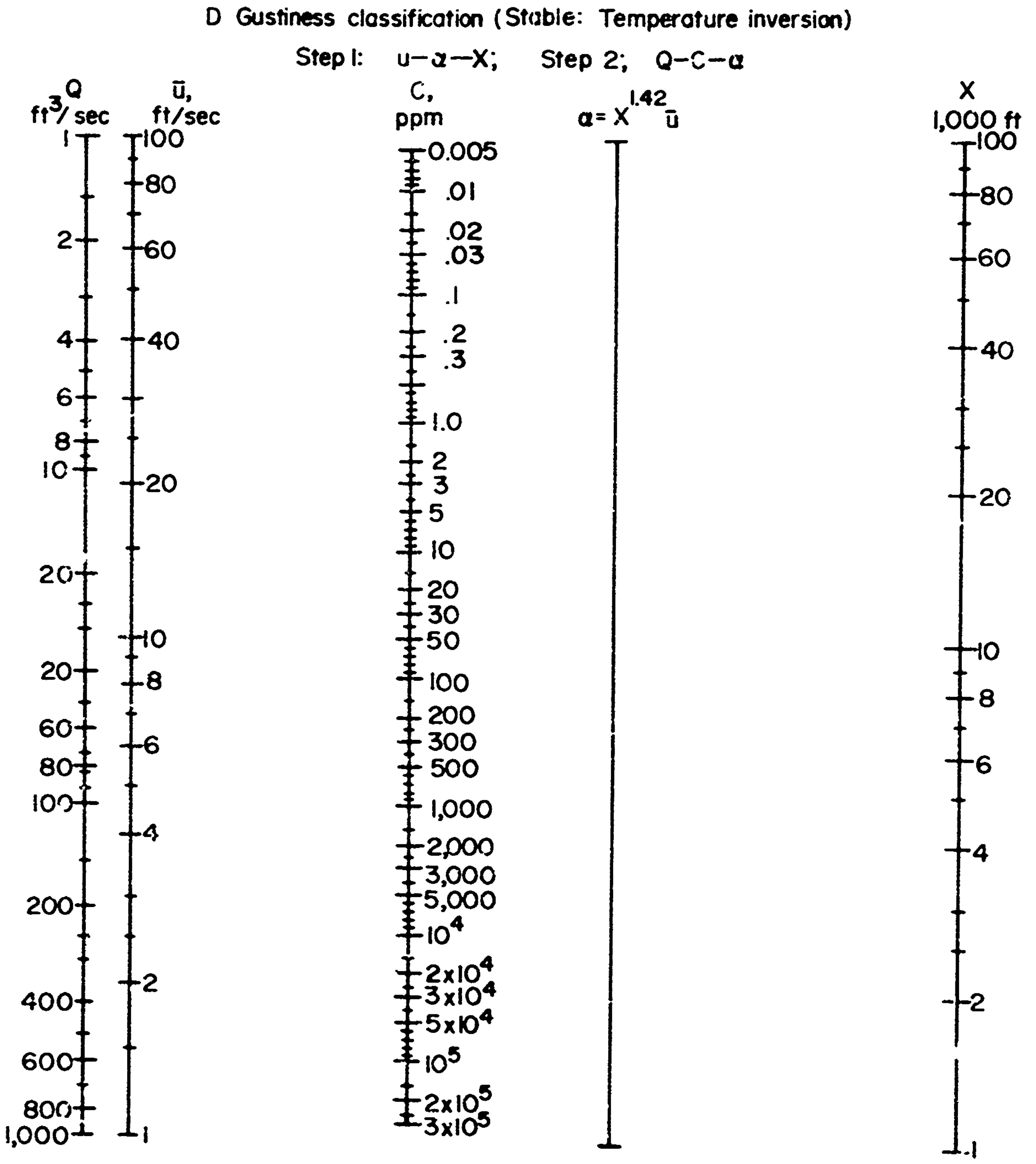
PGH-70191

Figure 21. - Elapsed times for gas cloud evolution in several experiments and computed times that a person would be exposed to 50 or 500 ppm chlorine in the same size spill.



PGH-70190

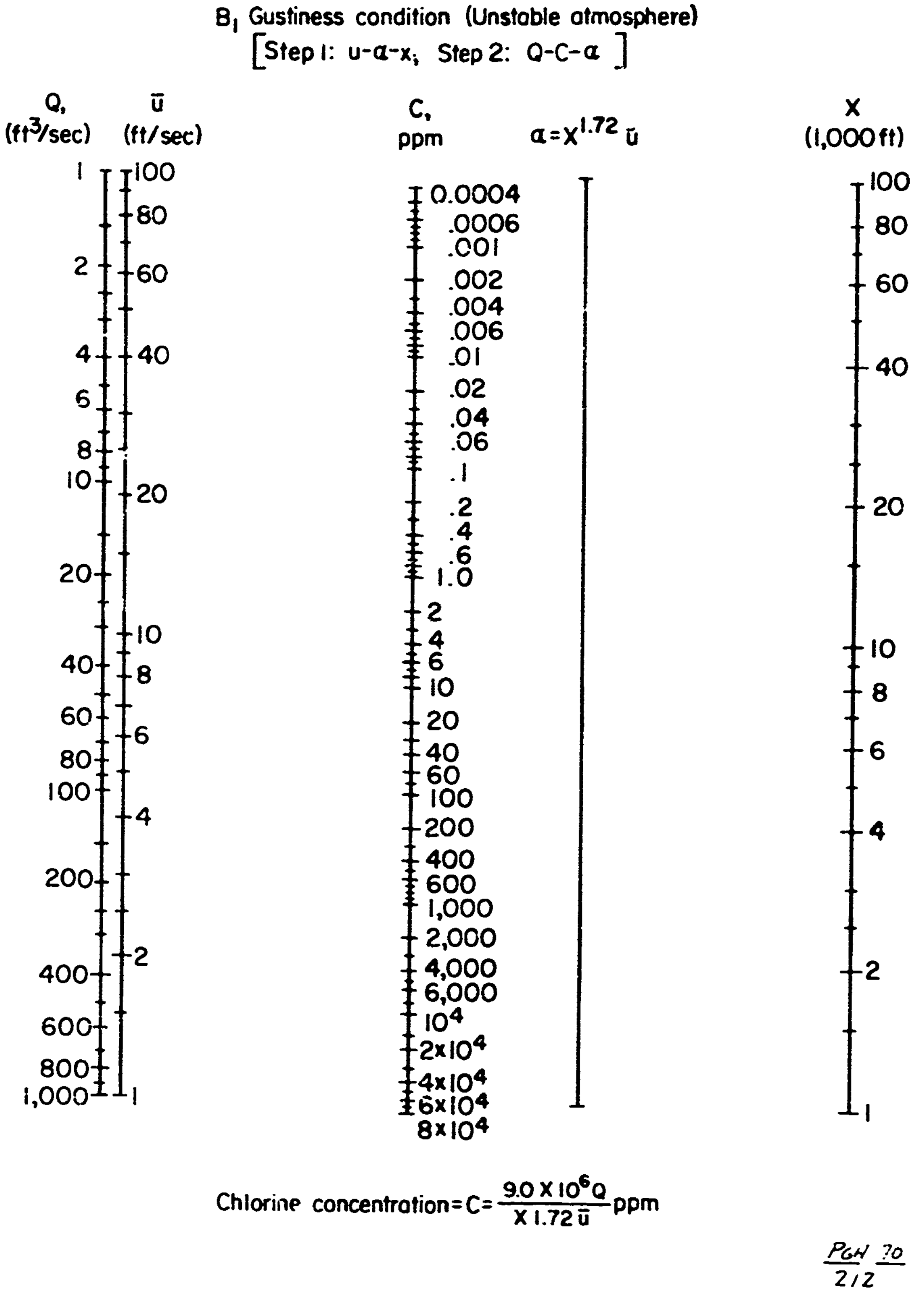
Figure 22. - Nominal distribution of chlorine concentration around an observation point downwind of an instantaneous release of gas.



Chlorine concentration $= C = \frac{8.3 \times 10^{6} Q}{X^{1.42} \bar{u}}$ ppm

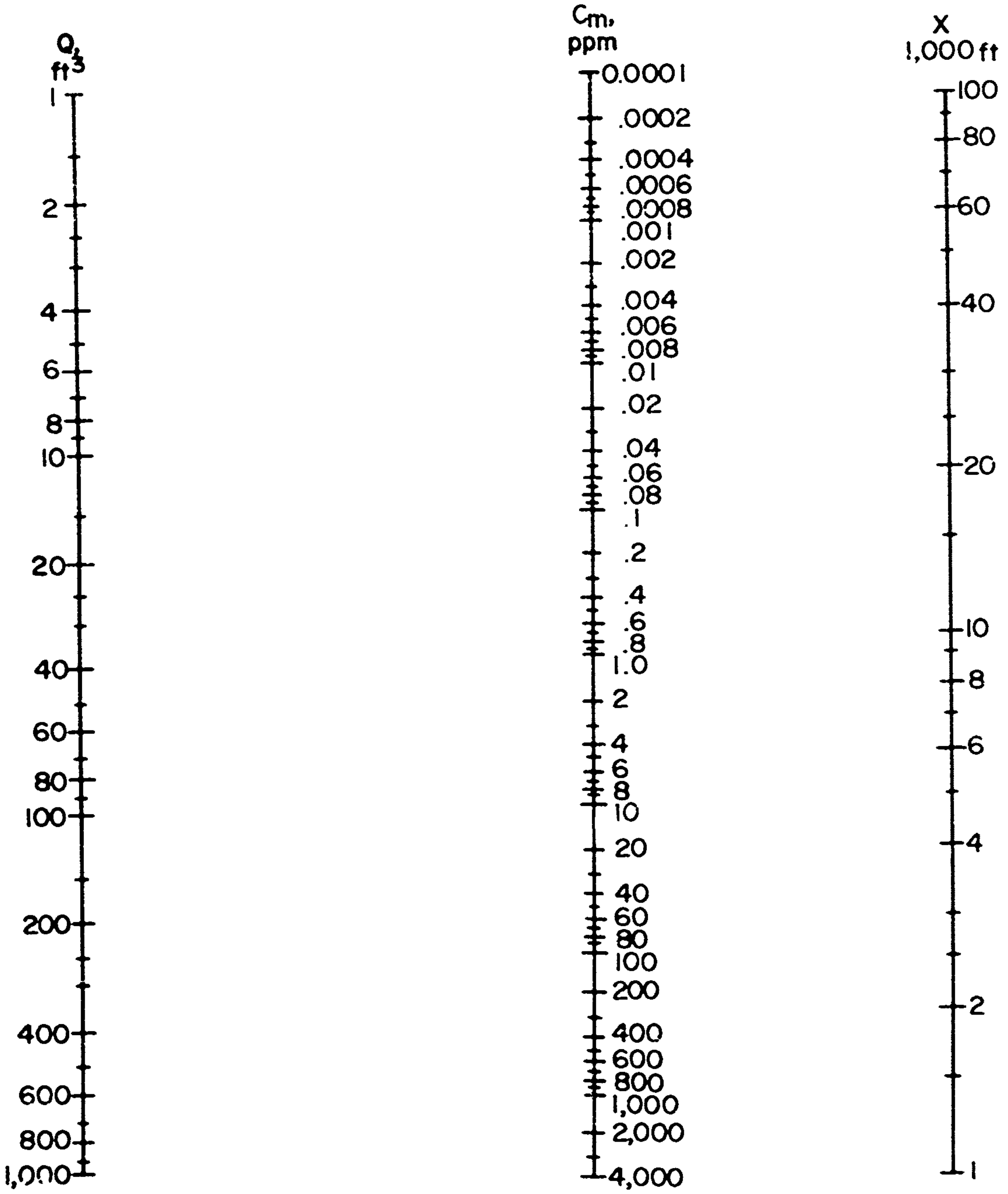
PaH-71
466

Figure 23. - Nomograph pertaining to concentrations from a steady source under stable atmospheric conditions.



PGH 70
2/2

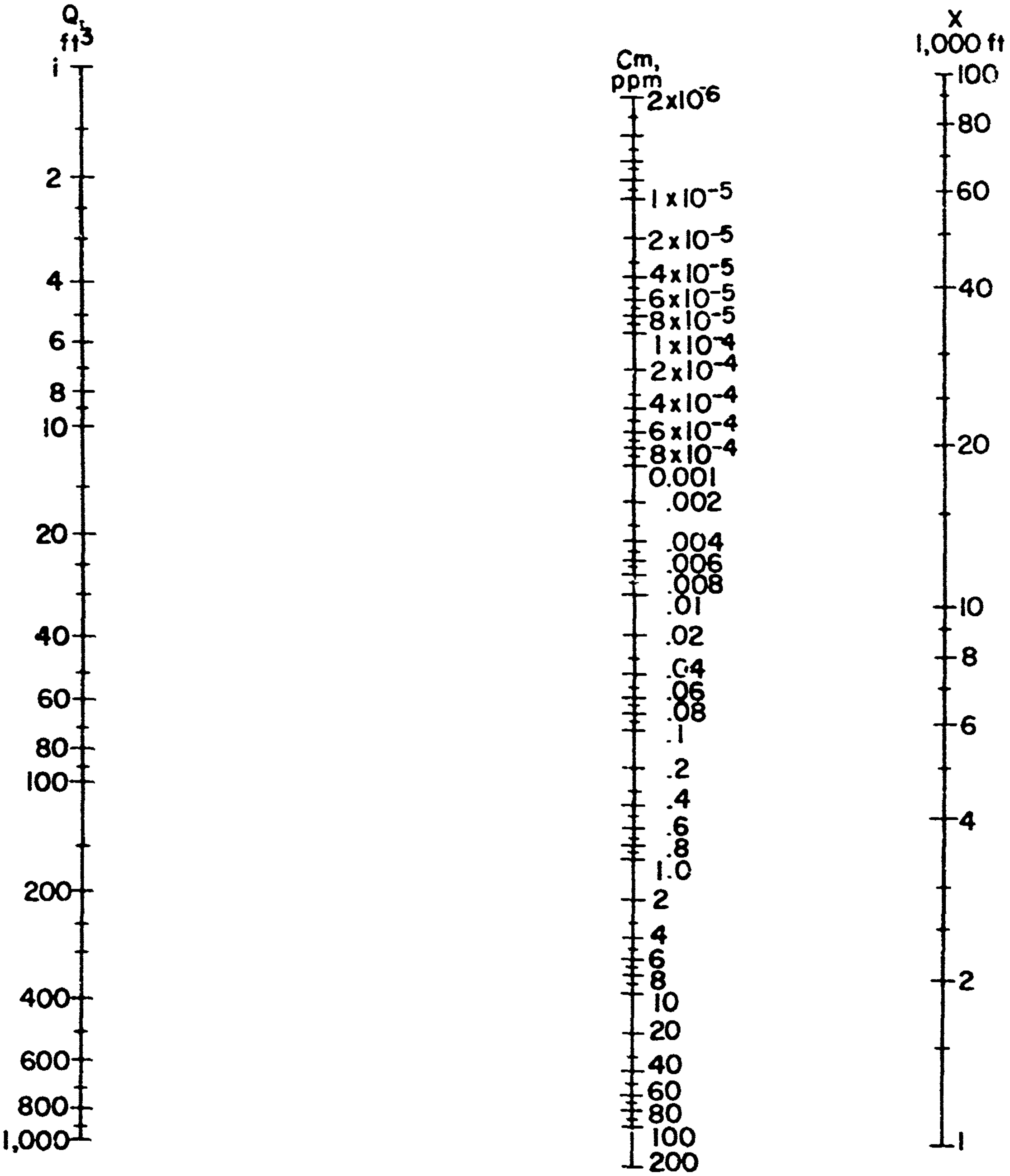
Figure 24. - Nomograph pertaining to concentrations from a steady source under unstable atmospheric conditions.



Chlorine concentration = $C_m = \frac{7.54 \times 10^6 Q}{x^{2.13}}$, ppm

BGN 71
465

Figure 25. - Nomograph pertaining to concentrations from an instantaneous release of gas under stable atmospheric conditions.



Chlorine concentration = $C_m = \frac{8.33 \times 10^6 Q}{X^{2.58}}$, ppm

P&W-70209

Figure 26. - Nomograph pertaining to concentration from an instantaneous release of gas under unstable conditions.

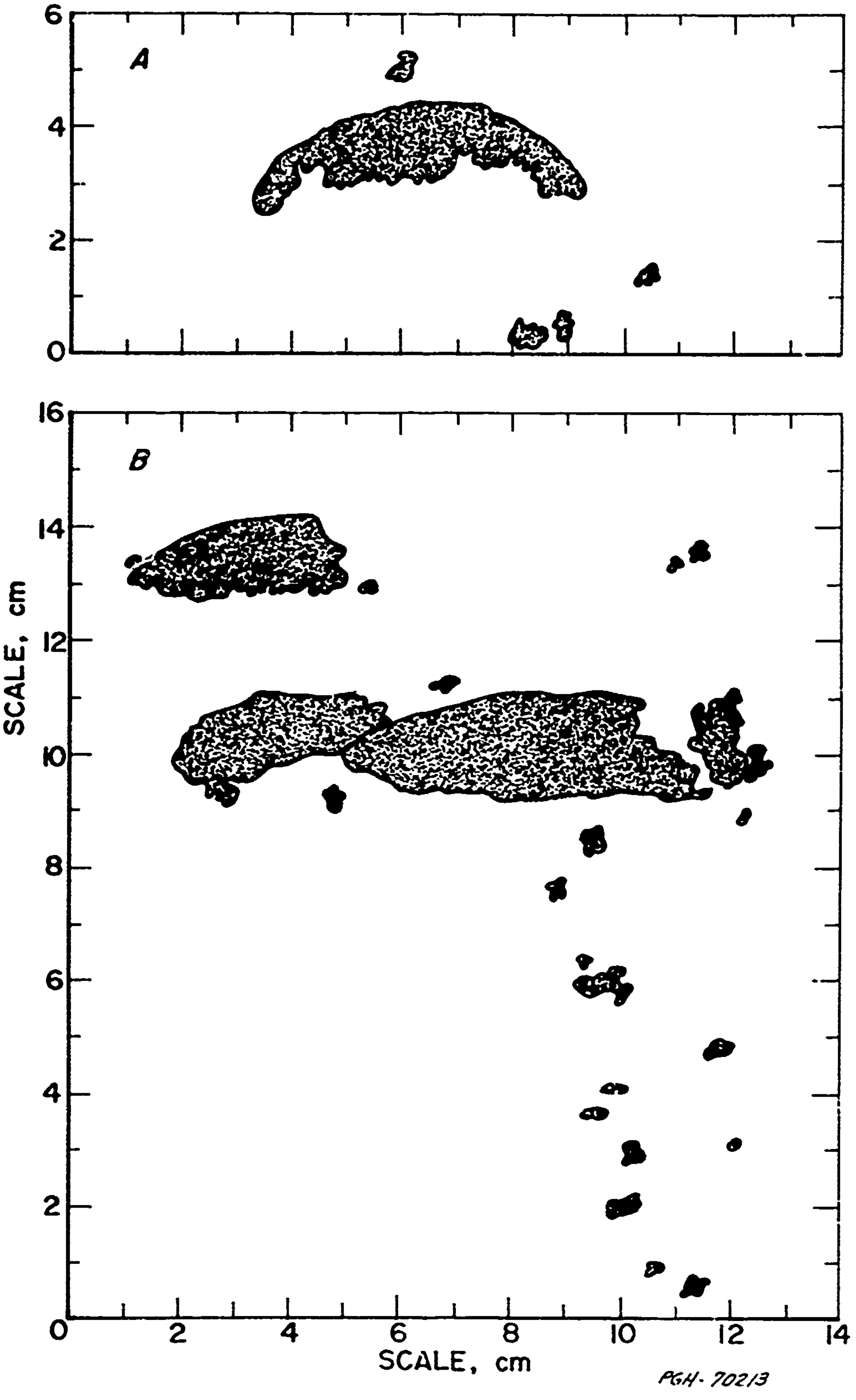


Figure 27. - Tracing of (a) 10 cc and (b) 30 cc chlorine bubble.