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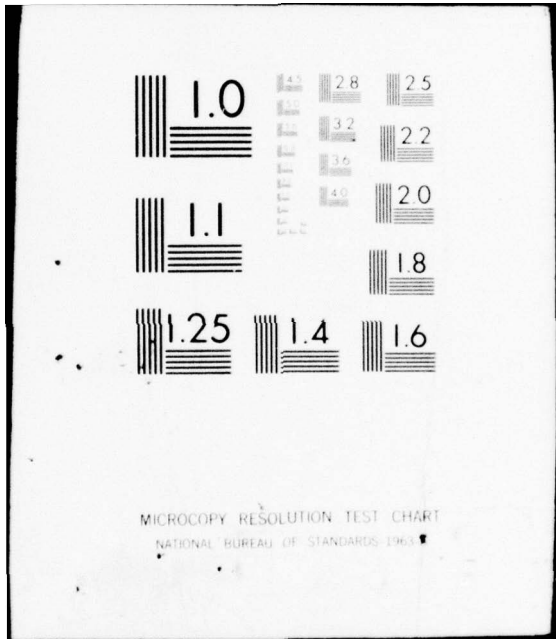
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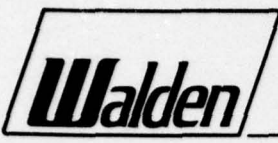
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EVALUATION OF OZONATION AND CHLORINATION
FOR DISINFECTION OF BLACKWATER

Final Report

Submitted by:

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PREFACE

This work was authorized and funded by the U.S. Army Mobility Equipment Research and Development Command under Contract No. DAAG53-76-C-0083. Technical guidance for this program was provided by Maurice Pressman, the Contracting Officer Technical Representative. The experimental aspects of the program were completed by Mr. Robert Allen of Walden.

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I. SUMMARY

Ozonation and chlorination were experimentally evaluated as alternative techniques for the disinfection of blackwater. The objective of the program was to provide a quantitative basis for assessing the relative advantages and disadvantages of these two techniques for the disinfection of blackwater generated on-board marine vessels prior to discharge to the navigable waters of the United States.

The experimental program focused primarily on determining the dosages of ozone and chlorine required at various temperatures (15°C and 30°C) and pH's (5-9). For ozonation neither the temperature nor the pH had a significant effect (at the 95% confidence level) on the required dosage. For chlorination the required dosage appeared to increase with temperature and pH (at 30°C only) but the correlations were not quite significant at the 95% confidence level. Most of the variability in the data appeared to result from the uncontrolled variability of the blackwater test samples and from other sources of experimental error.

The required ozone dosage was approximately three times as great as the required chlorine dosage for disinfection to a level of 200 fecal coliform colonies per 100 ml. For the blackwater samples tested, disinfection to the required level would be insured by application of an ozone dosage of 750 mg/l or a chlorine dosage of 240 mg/l; although for some samples the required dosages were considerably lower.

The estimated capital cost and operating cost for an ozonation system were both approximately three times as great as the corresponding costs for a chlorination system. However the absolute magnitude of the additional costs for an ozonation system do not appear to be excessive relative to other ship-board expenses. The final trade-off between the advantages of ozonation (no production of chlorinated hydrocarbons and more effective inactivation of viruses) and its cost disadvantage requires the application of subjective criteria beyond the scope of this program.

II. INTRODUCTION

The U.S. Army maintains a large number of marine vessels which have on-board sanitation devices for the collection, treatment, and discharge of blackwater (raw sewage diluted with flush water and mascerated to break up solids). The discharge of untreated blackwater to ports and navigable waterways could result in a human health hazard either directly or through the contamination of marine food supplies. In order to limit this type of pollution the U.S. Environmental Protection Agency has proposed standards⁽¹⁾ for sewage discharge from watercraft. These standards would limit the concentrations of fecal coliform bacteria and suspended solids in the discharged effluent. Two standards have been proposed: an interim standard (to become effective in 1977) and a final standard (to become effective in 1980). The proposed standards are:

	Max. Fecal Coliform Conc. (counts/100 ml)	Max. Suspended Solids Conc. (mg/l)
Interim	1000	no "visible floating solids"
Final	200	150

The interim standards can be met by treating the blackwater with a disinfectant such as chlorine or ozone before discharge. The final standards will require filtration in addition to disinfection.

The objective of this program was to compare chlorination and ozonation for the disinfection of blackwater. Both are effective disinfectants but each has particular advantages and disadvantages. The advantages of ozonation relative to chlorination include:

- Ozonation does not produce toxic chlorinated hydrocarbons;
- Ozonation is more effective for the inactivation of viruses.

The disadvantages of ozonation relative to chlorination include:

- Ozonation is more expensive for a given applied dosage;
- An ozonation system may be more sensitive to shock loadings.

In order to provide a basis for evaluating these advantages and disadvantages, an experimental investigation was undertaken to quantify the requirements of ozonation and chlorination for the disinfection of blackwater.

III. EXPERIMENTAL

A. TEST SYSTEMS AND OPERATING PROCEDURES

The system used for collection, storage, and transfer of blackwater is shown in Figure 1. The holding tank of the portable commode was charged with 9 gallons of tap water to which three separate contributions of solid waste were added along with a proportionate (but uncontrolled) number of liquid waste contributions. Following each contribution the commode was flushed by pumping blackwater from the holding tank to the bowl. Solids were dissipated by a maserator which was operated in tandem with the circulation pump. Following the third solid-waste contribution the three-way valve was turned to "discharge" and the contents of the commode holding tank were pumped into a 55 gal collection/storage tank.

A transfer pump (Gormann Rupp Model 81 1/2 D3-E 1/2) was used to withdraw a batch of waste from the storage tank. The tank was tipped back and forth in an attempt to mix the contents before withdrawing the waste. The suction of the pump was placed half-way between the liquid interface and the bottom of the tank, and the transfer required approximately thirty seconds. For earlier runs a separate batch of waste was withdrawn from the storage tank for each run; however for later runs a 10 gallon sample was withdrawn, mixed, and divided between an ozonation run and a chlorination run which were both conducted on the same day. This eliminated some of the variability that resulted from inaccuracies in withdrawing representative samples directly from the storage tank.

Waste was intermittently withdrawn from the collection/storage tank and fresh waste was intermittently added. It was hoped that this procedure would dampen some of the composition variations between individual waste contributions. On the other hand this procedure could lead to chemical and biochemical changes in the waste during storage. At one point during the test period a change in the nature of the waste was detected. At that point the contents of the collection/storage tank were discarded, and a second waste collection was initiated.

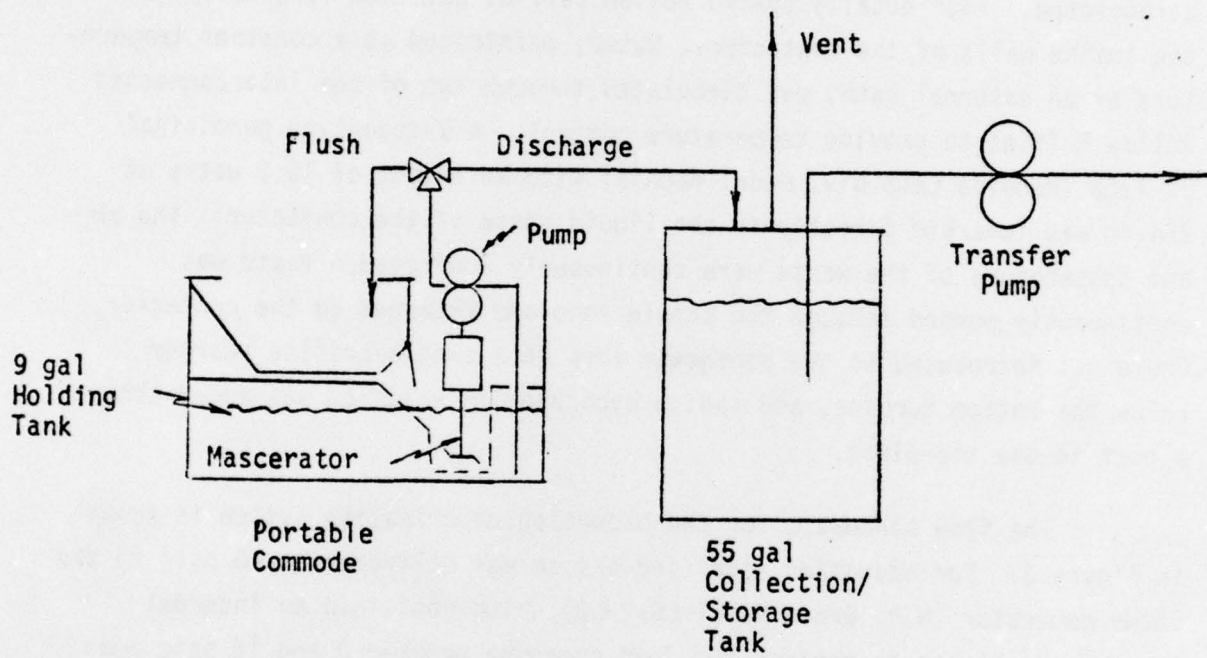


Figure 1: Waste Collection, Storage, and Transfer System

Ozonation and chlorination tests were conducted in a 14-liter fermenter (New Brunswick Scientific Model MMF-14) shown schematically in Figure 2. The envelope of the contactor was constructed of Pyrex glass; the top-plate and internals were constructed of stainless steel. The stirrer consisted of three turbine wheels, each containing six flat blades, mounted on a central shaft. The agitation speed was measured with a stroboscope. Four equally spaced hollow baffles extended vertically down the inside walls of the contactor. Water, maintained at a constant temperature by an external bath, was circulated through two of the interconnected hollow baffles to provide temperature control. A U-tube-type germicidal UV lamp (Hanovia Lamp Div. Model 688A45) with an output of 10.2 watts at 254 nm was immersed directly in the liquid phase of the contactor. The pH and temperature of the waste were continuously monitored. Waste was continuously pumped through the sample loop and returned to the contactor. Ozone was introduced to the contactor through a single-orifice sparger below the bottom turbine, and sodium hypochlorite solution was added through a port in the top-plate.

The flow schematic for the ozonation/chlorination system is shown in Figure 3. For ozonation, purified oxygen was delivered at 40 psig to the ozone generator (W.R. Grace Model LG-2-L2) which contained an internal pressure regulator to control the feed pressure between 0 and 15 psig and an internal flow meter to measure the output (10-100 SCFH). Ozone was generated in a corona discharge and delivered to the contactor through a check valve, a flow control valve, and a flow meter (0-3 SCFH). The bulk of the ozone was vented before the contactor since the generator produced much more ozone than required for the tests. A continuous chemiluminescent ozone monitor (TECO Model 10A NO_x monitor converted to monitor ozone) was used to monitor the ozone concentration in either the feed to the contactor or the off-gas from the contactor. A vacuum pump was used to draw the sample stream through a liquid trap, a cartridge filter, and the ozone monitor. The ozone monitor was calibrated using the potassium iodide absorption method described below.

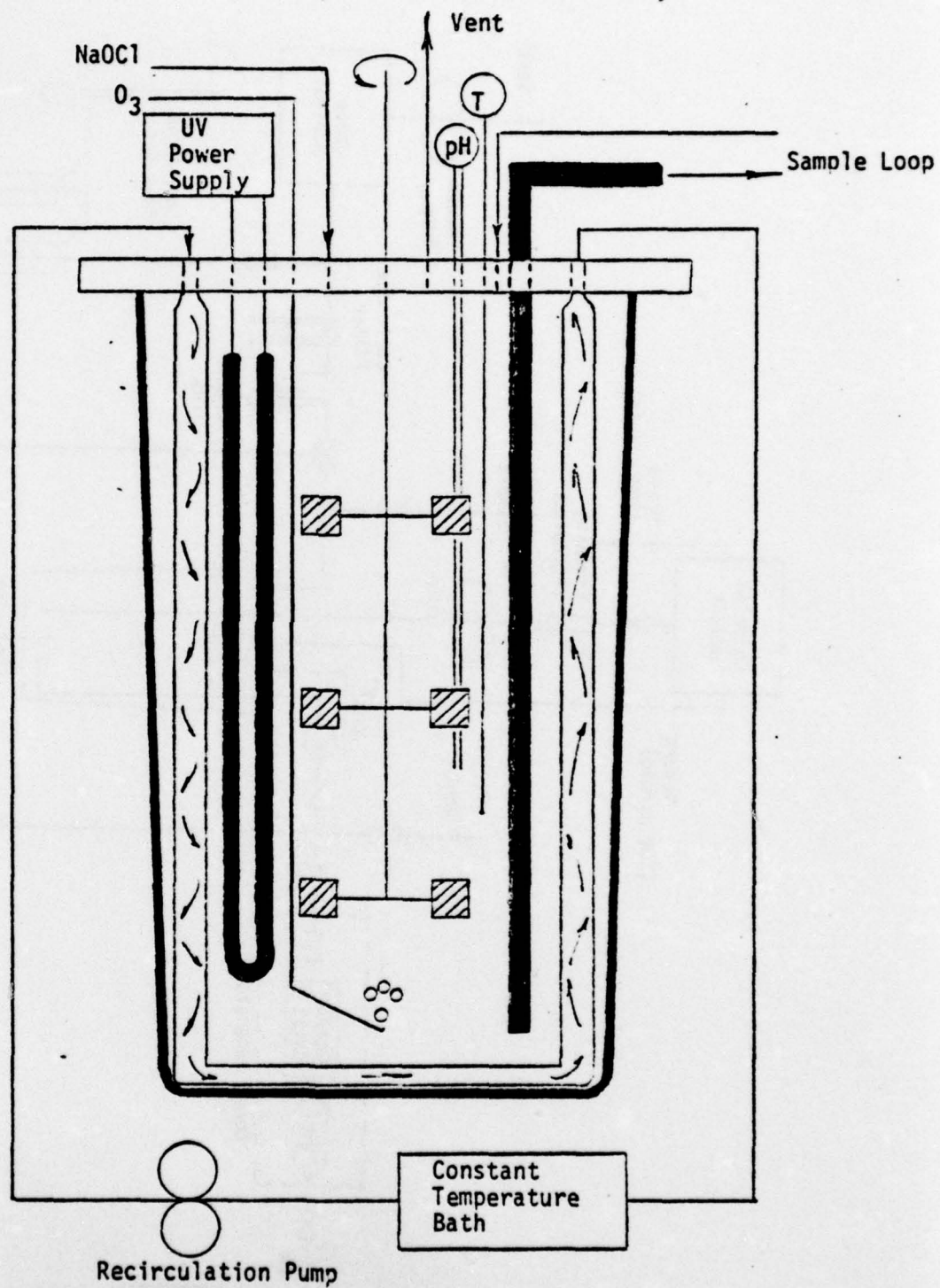


Figure 2: Schematic Diagram of Ozone/Chlorine Contactor

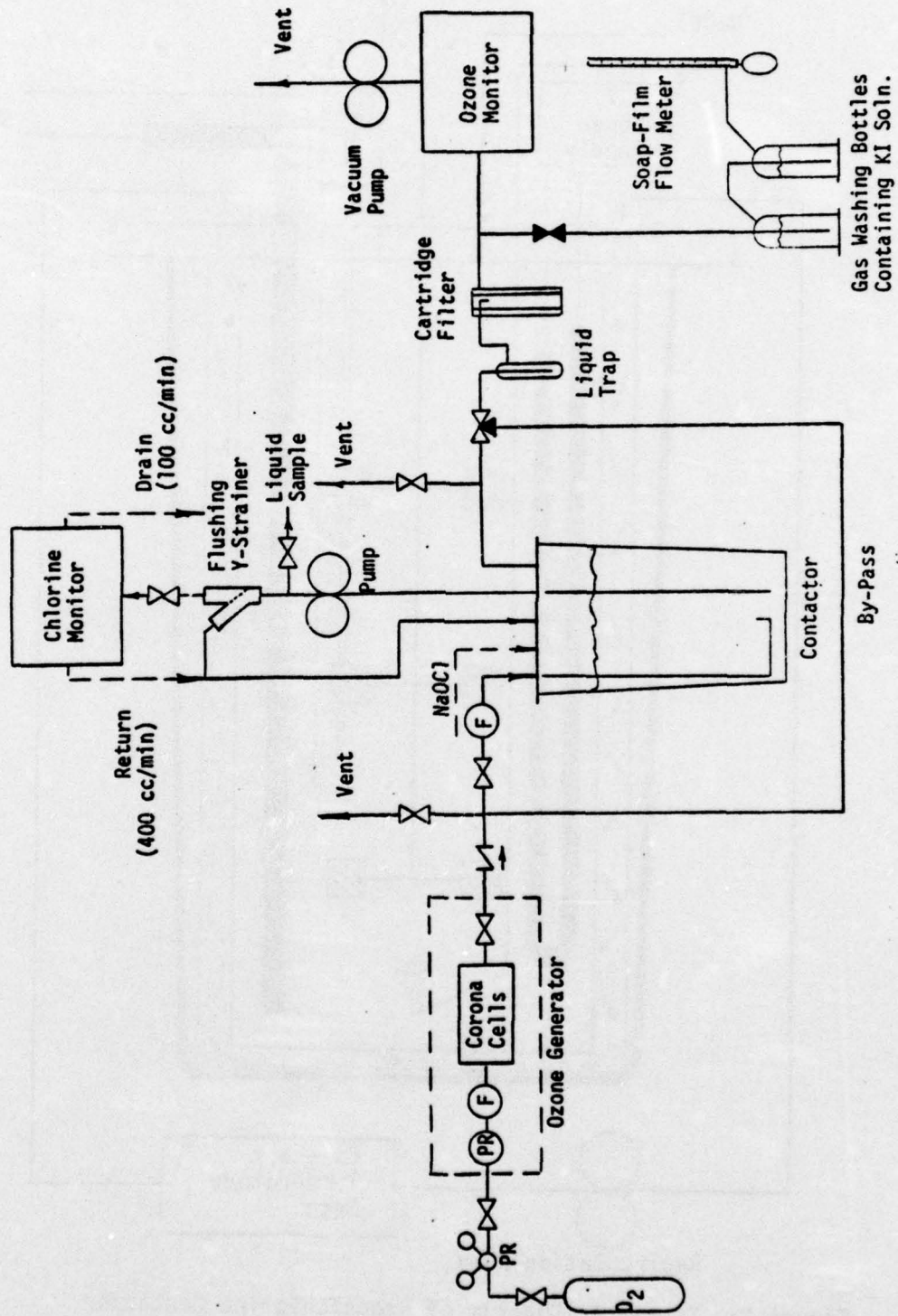


Figure 3: Flow Schematic for Ozonation/Chlorination System

During each test, waste from the contactor was pumped (Gormann Rupp Model 81 1/2 D3-E 1/2) through a sample loop and back to the contactor. Liquid samples were withdrawn from the discharge side of the pump.

For chlorination (dashed lines) sodium hypochlorite was injected into the contactor through a septum in the top-plate. A portion of the recirculated liquid stream flowed to a chlorine monitor (Capital Controls Model 872) which continuously measured the concentration of free available chlorine. A flushing "Y" strainer was used to prevent large particles from entering the chlorine monitor. Most of the stream passing through the chlorine monitor was returned to the sample loop, but a small portion (100 cc/min) which was mixed with a buffer solution for analysis was discarded.

A typical run was conducted by first charging the contactor with a batch of about 14 liters of blackwater. The recirculation pump in the liquid sample loop was activated; the waste was brought to the desired temperature; and the pH was adjusted to the desired level by injecting either HCl or NaOH into the waste. The agitation speed was increased to about 800 rpm and the initial liquid sample was taken.

For ozonation a flow of 2-3 SCFH of 1-2% wt O₃ in O₂ was sparged into the contactor. The ozone generator and monitor were warmed up and stabilized before the start of the run. The pH was readjusted as required during the run by injection of either acid or base.

For chlorination, a portion of recirculated liquid was passed through the chlorine monitor. A relatively large initial dose of chlorine (NaOCl solution containing 31 g/l of free available chlorine) was added to the contactor. The proper size of the initial dose was determined before the run in trial-and-error tests with a portion of the waste. Following the initial dose, smaller doses of chlorine were added as required to maintain the concentration of free available chlorine in the range of 1-3 mg/l.

B. SAMPLING AND ANALYSES

Six liquid samples were obtained during each test (at 0, 15, 30, 60, 90, and 120 min for ozonation and at 0, 3.25, 7.5, 15, 22.5, and 30 min for

chlorination). Analyses were performed for fecal coliform bacteria and total bacteria using Standard Methods⁽²⁾ assays 408B and 406, respectively. In later tests the total bacteria analyses were dropped since the proposed standards do not include limitations on total bacteria and since the concentration trends were similar for total bacteria and fecal coliform bacteria.

Residual concentrations of free available chlorine ($\text{Cl}_2 + \text{HOCl} + \text{OCl}^-$) were monitored continuously, and 14 readings were recorded periodically during the run. The chlorine monitor employs an amperometric technique to detect chlorine following pH adjustment to 4.0-4.5 by addition of a sodium acetate-acetic acid buffer.

Ozone concentrations in the contactor feed and effluent were monitored during the ozonation runs. The ozone level was determined by measuring the light emission from the chemiluminescent reaction between ozone and NO.

C. INSTRUMENT CALIBRATION

The chlorine monitor was factory calibrated before shipment using the amperometric titration technique (Standard Methods⁽²⁾ assay 114B).

The ozone monitor was calibrated using the simplified procedure recommended by the manufacturer of the ozone generator⁽³⁾. The procedure consists of absorbing a known flow rate of ozone for a fixed time in a solution containing excess potassium iodide. The ozone quantitatively oxidizes I^- to I_2 which remains complexed in solution as I_3^- (yellow). After acidification the solution is titrated with a standardized solution of sodium thiosulfate which reduces I_2 to I^- (clear end point).

The feed flow meter for the ozone feed gas was calibrated against a soap-film flow meter.

D. DATA REDUCTION

The procedures used to reduce the data are given in Appendix A along with sample calculations for both ozonation and chlorination.

IV. EXPERIMENTAL RESULTS

A total of 17 ozonation tests and 14 chlorination tests were conducted using the experimental systems and procedures described above. Temperatures of 15 and 30°C were investigated to indicate the effect of typical water-temperature variations, and pH's from 5 to 9 were investigated to indicate the effect of pH within a reasonable range. In addition the effect on ozonation of irradiation with UV light was investigated. The results obtained are described below and are discussed in more detail in the following section (Discussion of Results).

A. VARIATIONS IN BLACKWATER COMPOSITION

Table 1 gives the test chronology and the initial fecal coliform concentrations for the ozonation and chlorination tests. Considerable variability was observed in the initial fecal coliform concentrations: concentrations, in colonies per 100 ml, ranged from 3.5×10^5 for Run C-3 to 3.0×10^8 for Run O-10. There are several potential sources of this variability:

- 1) addition of waste of different composition to the storage tank,
- 2) changes in waste composition during storage,
- 3) removal of an unrepresentative test batch from the storage tank,
- 4) removal of an unrepresentative sample from the reactor for the initial concentration analysis, and
- 5) removal of an unrepresentative aliquot from the sample bottle for analysis.

The first two sources of variability involve time-dependent changes in the waste; the last three involve sampling errors.

Time-dependent changes in the initial fecal coliform concentrations do not appear to be significant. However, other changes to be described below did occur, and after the runs conducted on 4/5 the blackwater storage tank was emptied, and a second collection was initiated for the runs of 4/12 through 4/22. To determine whether or not the variability was time related, a straight-line regression analysis was performed for log (Initial F. Coli.

TABLE 1
TEST CHRONOLOGY AND INITIAL FECAL COLIFORM CONCENTRATIONS

Date	Ozonation Run No.	Log of Initial F. Coli Conc.	Chlorination Run No.	Log of Initial F. Coli Conc.
3/4	0-1	6.89	--	--
3/10	--	--	C-1	6.26
3/11	--	--	C-2	6.11
3/15	0-2	6.93	C-3	5.54
3/16	0-3	8.27	C-4	7.62
3/17	0-4	8.34	--	--
3/22	0-5	7.34	--	--
3/22	0-6	8.26	--	--
3/23	0-7	8.04	C-5	5.84
3/24	0-8	8.08	C-6	8.18
3/31	0-9	6.76	C-7	6.79
4/5	0-10	8.48	C-8	7.04
4/12*	0-11	7.75	C-9	7.78
4/13*	0-12	7.84	C-10	7.72
4/14*	0-13	6.93	C-11	6.84
4/14*	0-14	7.90	C-12	6.96
4/15*	0-15	7.98	--	--
4/21*	0-16	7.85	C-13	7.95
4/22*	0-17	7.77	C-14	7.86

*Single batch removed from blackwater storage tank and divided between ozonation and chlorination run.

Conc.) versus days after first run. The regression slopes were slightly positive but the 95% confidence intervals for the slopes included zero slope for data both before and after the point at which the blackwater storage tank was emptied. Thus the data are consistent with the hypothesis that no significant long-term changes in the initial fecal coliform concentrations occurred with time.

On the other hand short-term variations were significant. Tests run on the same day (e.g. Runs 0-7 and C-5) and on successive days (e.g. Runs C-5 and C-6) could have widely different initial concentrations. This can be attributed to one or more of the last three sources of variability listed above. For runs conducted with the second blackwater storage batch (4/12 through 4/22) a single batch was removed from the storage tank and divided between the ozonation run and the chlorination run for that day. With the exception of one day (4/14) the initial concentrations for the runs conducted on the same day agreed to within 32%. Therefore it is likely that much of the variability in the initial fecal coliform concentrations resulted from problems in withdrawing representative test batches from the storage tank.

B. OZONATION RESULTS

Typical ozonation results are shown in Figure 4 (Run 0-1 conducted at a pH of 9.0 and a temperature of 30°C). The logarithm of microorganism concentration, in colonies per 100 ml for fecal coliform (circles) and counts per ml for total bacteria (triangles), is plotted against the ozone dosage in mg ozone per liter of blackwater. The data indicate a linear decrease of log (F. Coli. conc.) with increasing ozone dosage. The straight line shown in Figure 1 was fit to the data by the method of least squares and gives a linear regression correlation coefficient of -0.978. The total bacteria analyses show a similar linear decrease.

The linear relationship between log (F. Coli. conc.) and ozone dosage was observed for all ozonation runs. Correlation coefficients ranged from -0.869 to -0.993. Figure 5 shows the results for the run with

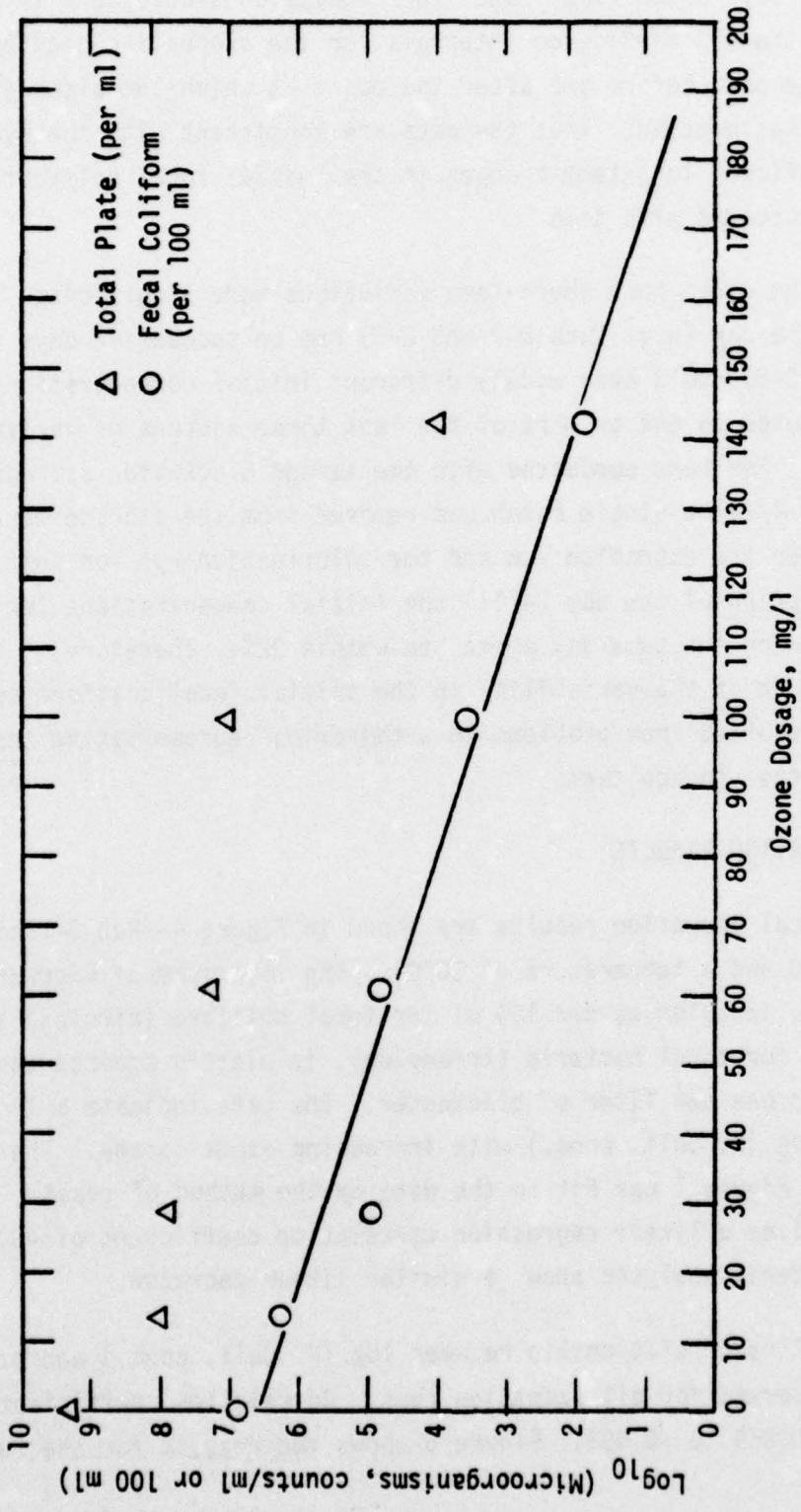


Figure 4: Ozone Disinfection of Blackwater at 30°C, pH 9, and no UV

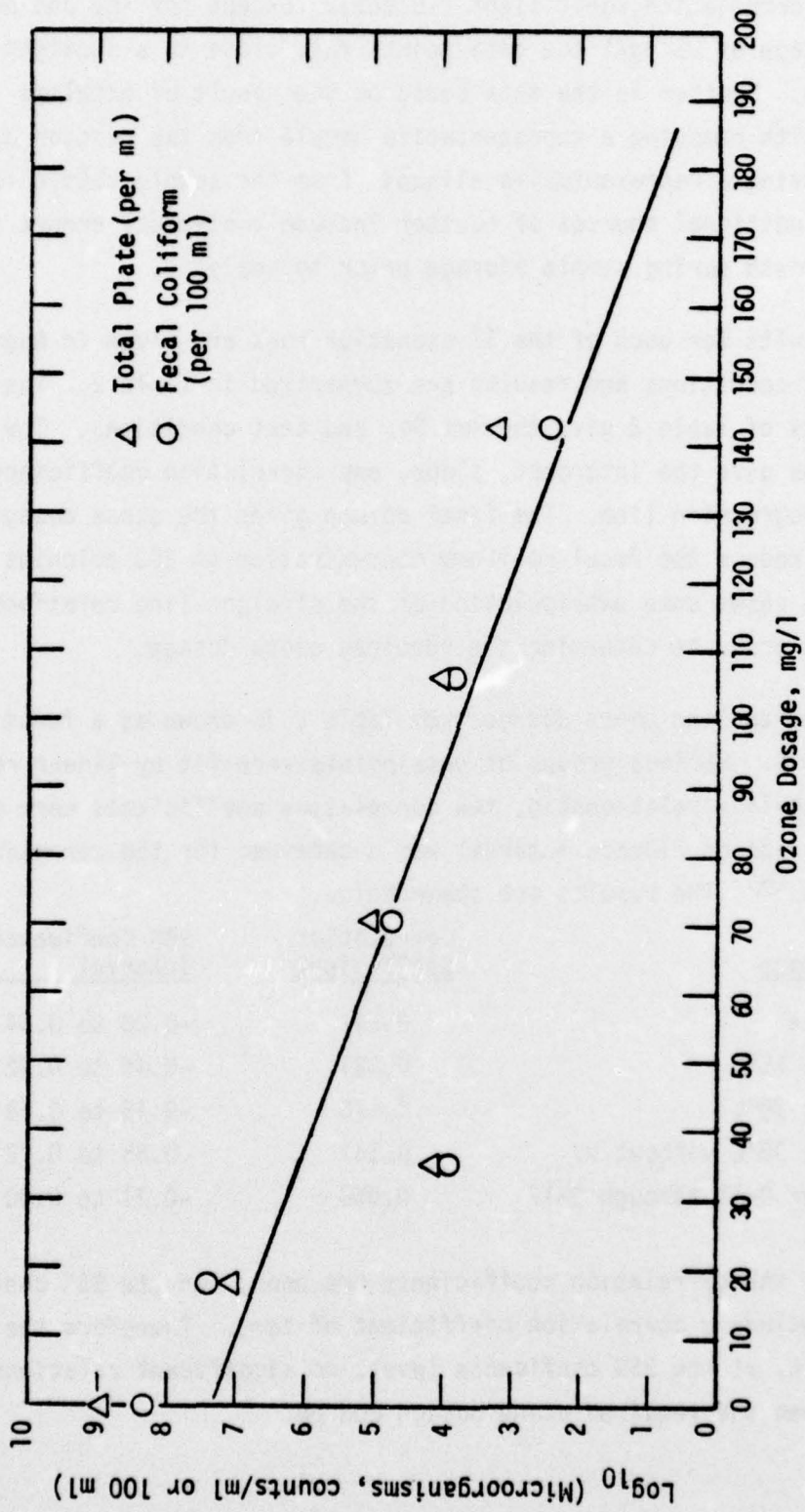


Figure 5: Ozone Disinfection of Blackwater at 30°C, pH 5, and No UV

the poorest correlation coefficient (-0.869). Except for the one point at an ozone dosage of 35 mg/l the data points fall close to a straight-line relationship. Scatter in the data could be the result of problems associated with removing a representative sample from the reactor during a run and removing a representative aliquot from the sample bottle for analysis. Additional sources of scatter include analytical errors and bacterial growth during sample storage prior to analysis.

Results for each of the 17 ozonation runs are given in Appendix B. The test conditions and results are summarized in Table 2. The first three columns of Table 2 give the Run No. and test conditions. The next three columns give the intercept, slope, and correlation coefficient for the fitted regression line. The final column gives the ozone dosage required to reduce the fecal coliform concentration to 200 colonies per 100 ml. In most cases some extrapolation of the straight-line relationship was necessary in order to determine the required ozone dosage.

The required ozone dosage from Table 2 is shown as a function of pH in Figure 6. Various groups of data points were fit by linear regression to a straight-line relationship, the correlation coefficients were determined, and a 95% confidence interval was determined for the correlation coefficients.⁽⁴⁾ The results are shown below.

<u>Data Group</u>	<u>Correlation Coefficient</u>	<u>95% Confidence Interval</u>
All Data	0.241	-0.28 to 0.64
Data at 15°C	0.521	-0.45 to 0.92
Data at 30°C	0.175	-0.45 to 0.68
Data at 30°C without UV	0.147	-0.55 to 0.72
Data for 0-11 through 0-17	0.558	-0.31 to 0.90

In all cases the correlation coefficients are poor, and the 95% confidence intervals include a correlation coefficient of zero. Therefore the data indicate that, at the 95% confidence level, no significant relationship exists between the required ozone dosage and pH.

TABLE 2
SUMMARY OF OZONATION TEST CONDITIONS AND RESULTS

Run	Temp., °C	pH	Linear Regression of log (F. Coli. Conc.) vs. O ₃ Dosage			Required ^(a) O ₃ Dosage (mg/l)
			Intercept	Slope	L.R. Coeff.	
0-1	30	9	6.5744	-0.03219	-0.9784	133
0-2	15	5	6.9297	-0.03406	-0.9646	136
0-3	15	7	8.7068	-0.02880	-0.9526	222
0-4	30	5	7.3491	-0.03600	-0.8686	140
0-5 ^(b)	30	5	7.4010	-0.01360	-0.9891	375
0-6	30	7	8.5710	-0.01844	-0.9448	340
0-7 ^(b)	30	7	7.9997	-0.03279	-0.9393	174
0-8	15	9	8.3165	-0.01803	-0.8962	334
0-9	30	7 ^(c)	6.6474	-0.00807	-0.9330	538
0-10	30	7 ^(c)	8.3483	-0.00604	-0.8838	1001
0-11	30	7.6 ^(c)	8.1694	-0.01360	-0.9249	432
0-12	15	8 ^(c)	8.0858	-0.01480	-0.9696	391
0-13	15	6	7.2187	-0.01046	-0.9250	470
0-14	30	6	7.6717	-0.01260	-0.9267	426
0-15	15	8.5 ^(c)	8.0358	-0.01030	-0.9927	557
0-16	30	8.2 ^(c)	7.5536	-0.01169	-0.9467	449
0-17	30	9	7.4695	-0.00770	-0.9073	671

a) Dosage required to reduce fecal coliform concentration to 200 counts/100 ml

b) UV light on during run

c) Run conducted at natural pH of waste; no pH adjustment

NOTE: Following run 0-10 the blackwater storage tank was emptied.
A fresh batch of waste was collected for runs 0-11 through 0-17.

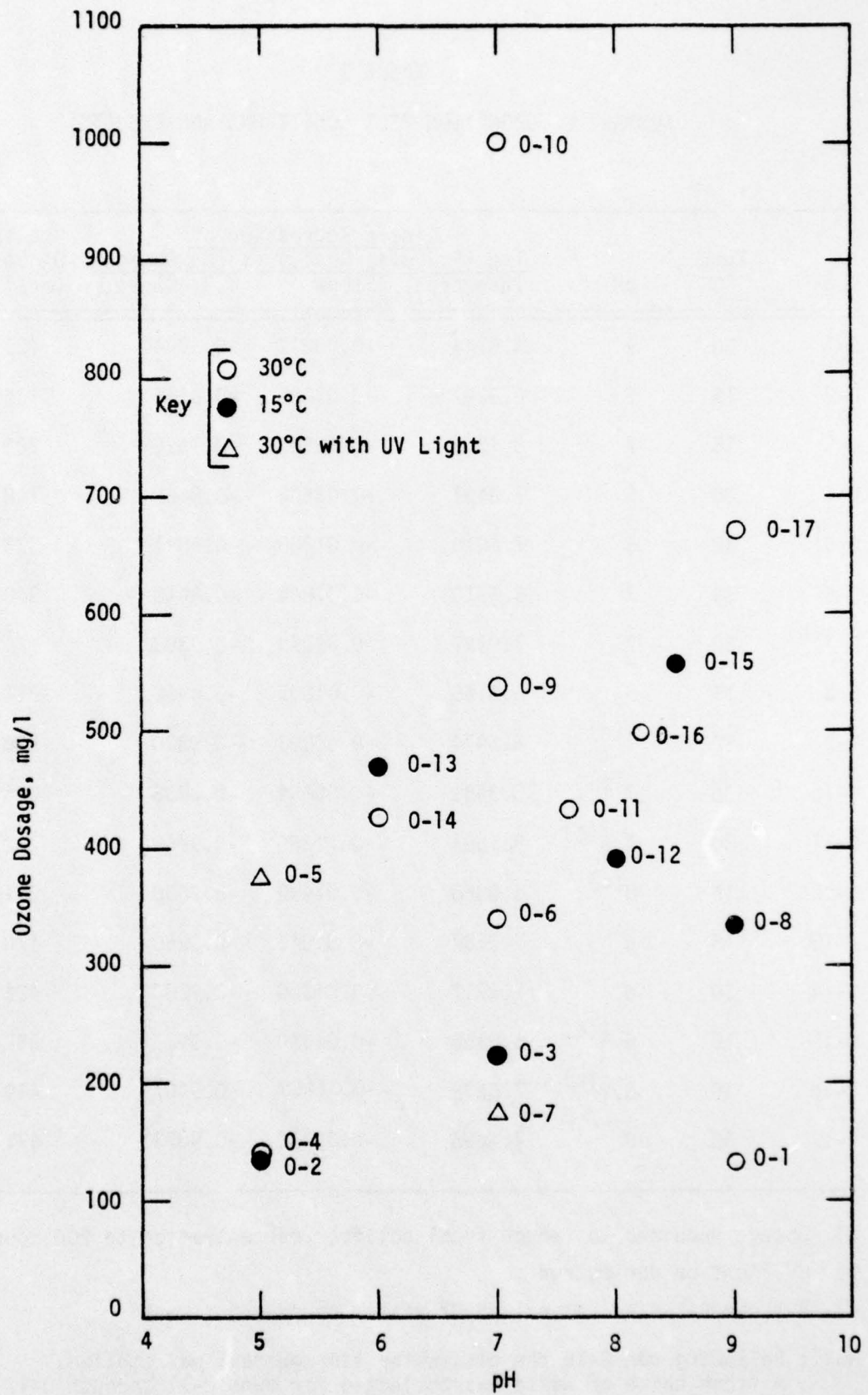


Figure 6: Required Ozone Dosage vs. pH for Disinfection of Blackwater to 200 Fecal Coliform Colonies per 100 ml.

The effect of UV irradiation was investigated at 30°C and 2 pH's. At pH 5 the required dosage with UV irradiation (Run 5) was substantially greater than without UV irradiation (Run 4). However at pH 7 the required dosage with UV irradiation (Run 7) was substantially less than without UV irradiation (Run 6). Therefore, for the limited extent to which the effect of UV irradiation was investigated, no consistent effect on dosage was observed.

During the ozonation tests it became increasingly difficult to reduce the bacterial count. This is shown in Figure 7 in which the required ozone dosage (to reach 200 fecal coliform colonies/100 ml) is plotted against the time, in days, from which the first run was conducted. The abscissa of Figure 7 gives an indication of the age of the blackwater waste although fresh waste was being added during this test period. The required ozone dosage increased gradually over the first 20 days of testing but began to increase rapidly thereafter. Runs 0-9 and 0-10 were conducted, respectively, at 27 and 32 days after the first run and required significantly higher ozone dosages for fecal coliform reduction. As shown in Table 1 the initial fecal coliform concentrations for Runs 0-9 and 0-10 were not significantly higher than for previous runs. Therefore the increase in ozone requirement was not associated with an increase in bacterial concentration. However, some change in the composition of the blackwater did occur as evidenced by a pH change from a value of about 8.0 for earlier runs to a value of 7.0 for Runs 0-9 and 0-10. Because of this change the contents of the blackwater storage tank were discarded following Run 0-10 and a new collection was started.

The remainder of the tests (Runs 0-11 through 0-17) were conducted with the second waste collection. The pH of this collection remained at about 8.0 for the duration of the tests. The required ozone dosage for the initial tests with the second waste collection were in the range of 400-500 mg/l compared to a requirement of 100-200 mg/l for the initial tests of the first waste collection. This difference is probably due to differences in the nature of the wastes. However, as shown in Table 1, the higher ozone

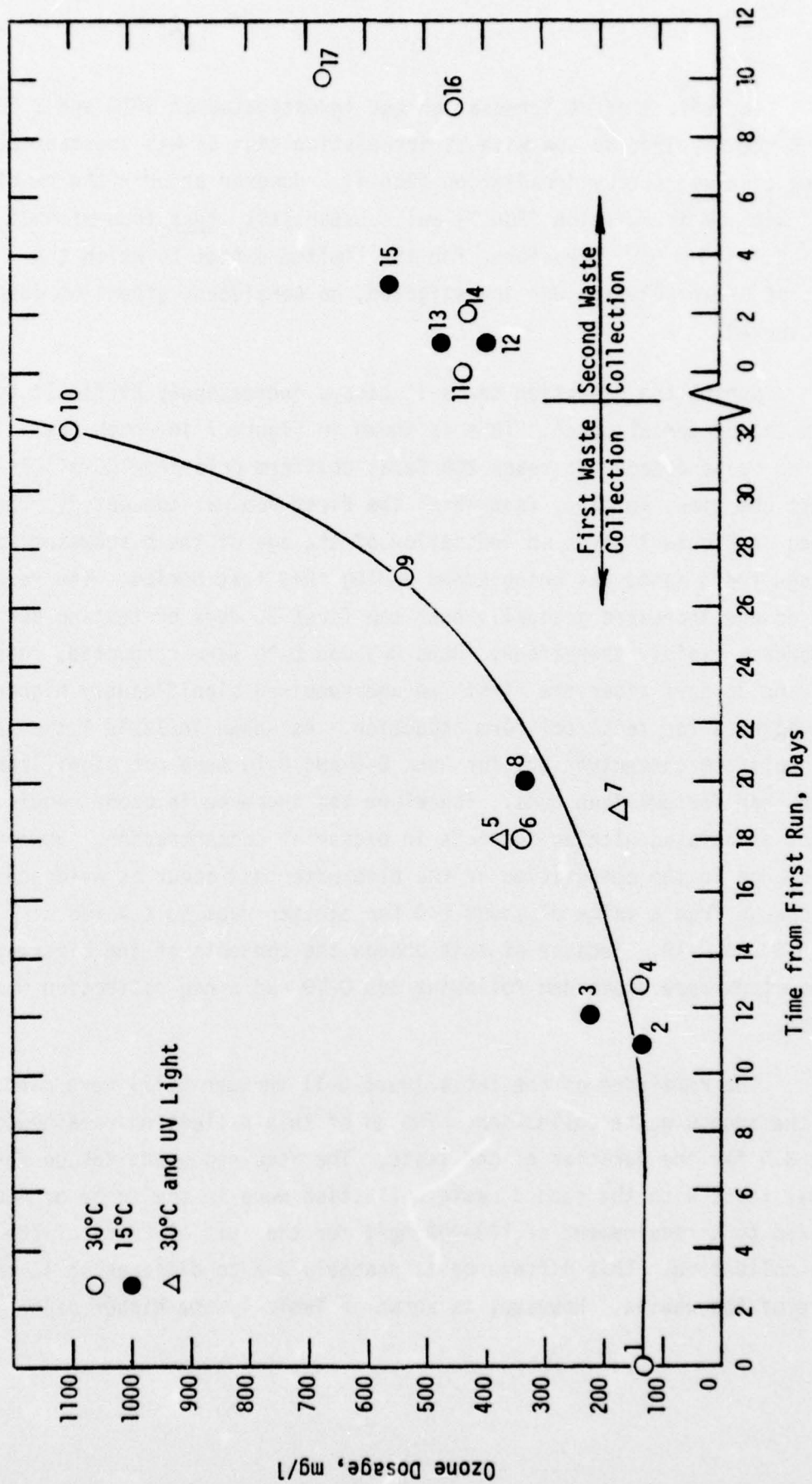


Figure 7: Required Ozone Dosage vs. Time from Start of Tests for Disinfection of Blackwater to 200 Fecal Coliform Colonies/100 ml.

dosage required for the second waste collection is not the result of a significantly higher bacterial concentration in the waste.

Based on the fitted regression line for the data obtained with the second waste collection, it would appear that the ozone requirement again increases gradually with storage time. However the correlation coefficient (0.651) has a 95% confidence interval (-0.18 to 0.93) which includes a correlation coefficient of zero. Therefore, at the 95% confidence level, the data are consistent with the hypothesis that there is no increase in ozone requirement with storage time. That is, the positive slope of the line can be explained in terms of experimental scatter.

C. CHLORINATION RESULTS

Typical chlorination results are shown in Figures 8 and 9. The logarithm of the fecal coliform concentration (in colonies per 100 ml) is plotted against the contact time (in minutes). Most of the data could be correlated with a single line as shown in Figure 8. However, for five of the 14 chlorination runs two straight-line segments of different slope, as shown in Figure 9, were required to correlate the data. The solid straight lines shown in Figures 8 and 9 were fit to the fecal coliform data points (circles) by the method of least squares. The data for total bacteria (see Appendix C) indicate a similar logarithmic decrease with increasing operating time.

The chlorine dosage (squares) is also plotted against the contact time in Figures 8 and 9. The bulk of the chlorine dose was added at the beginning of the run and periodic chlorine additions were made during the run to keep the free available chlorine residual within the desired range. In general a good linear relationship was obtained between the chlorine dosage and the contact time. The dashed lines of Figures 8 and 9 were fit to the data points by the method of least squares.

The results for each of the chlorination runs are given in Appendix C. The test conditions and results are summarized in Table 3. The first

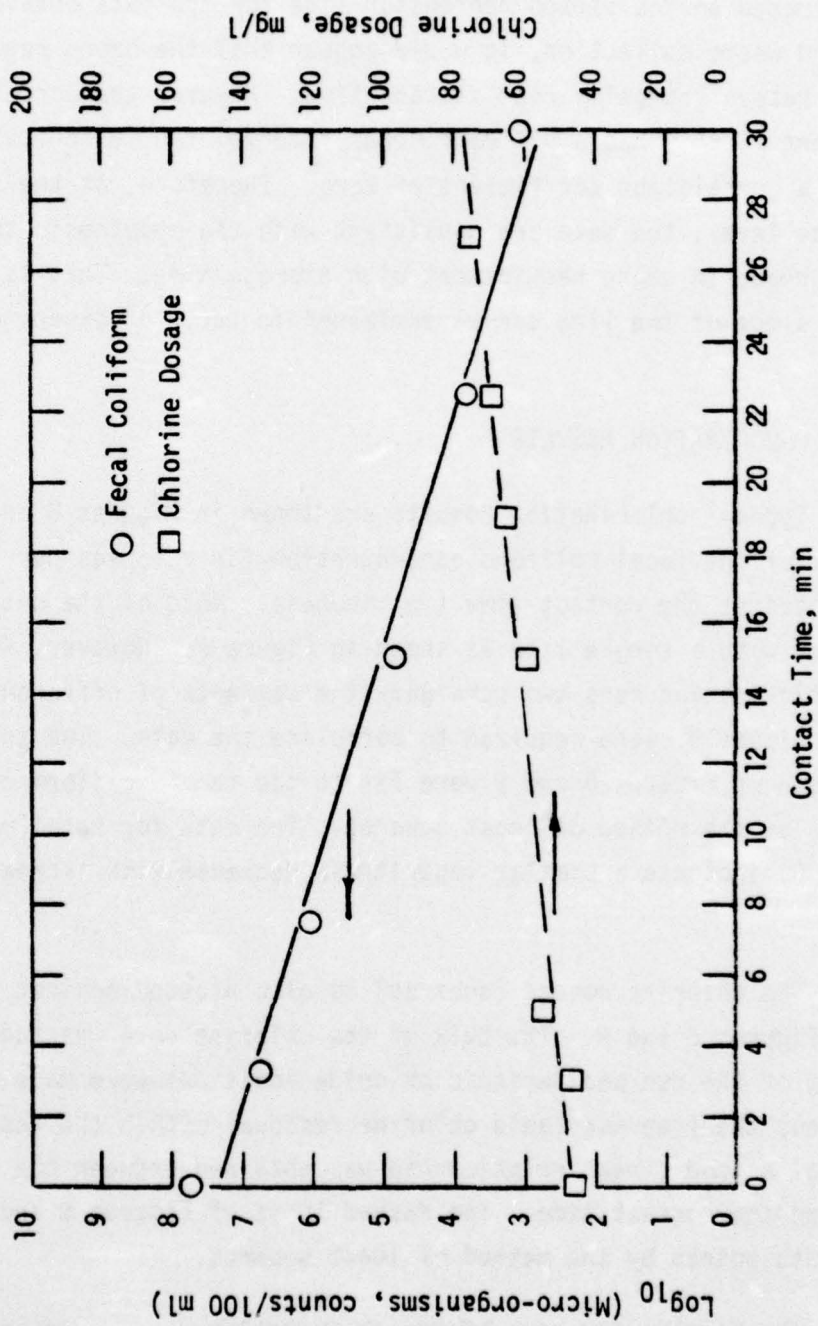


Figure 8: Chlorine Disinfection of Blackwater at 15°C and pH 8

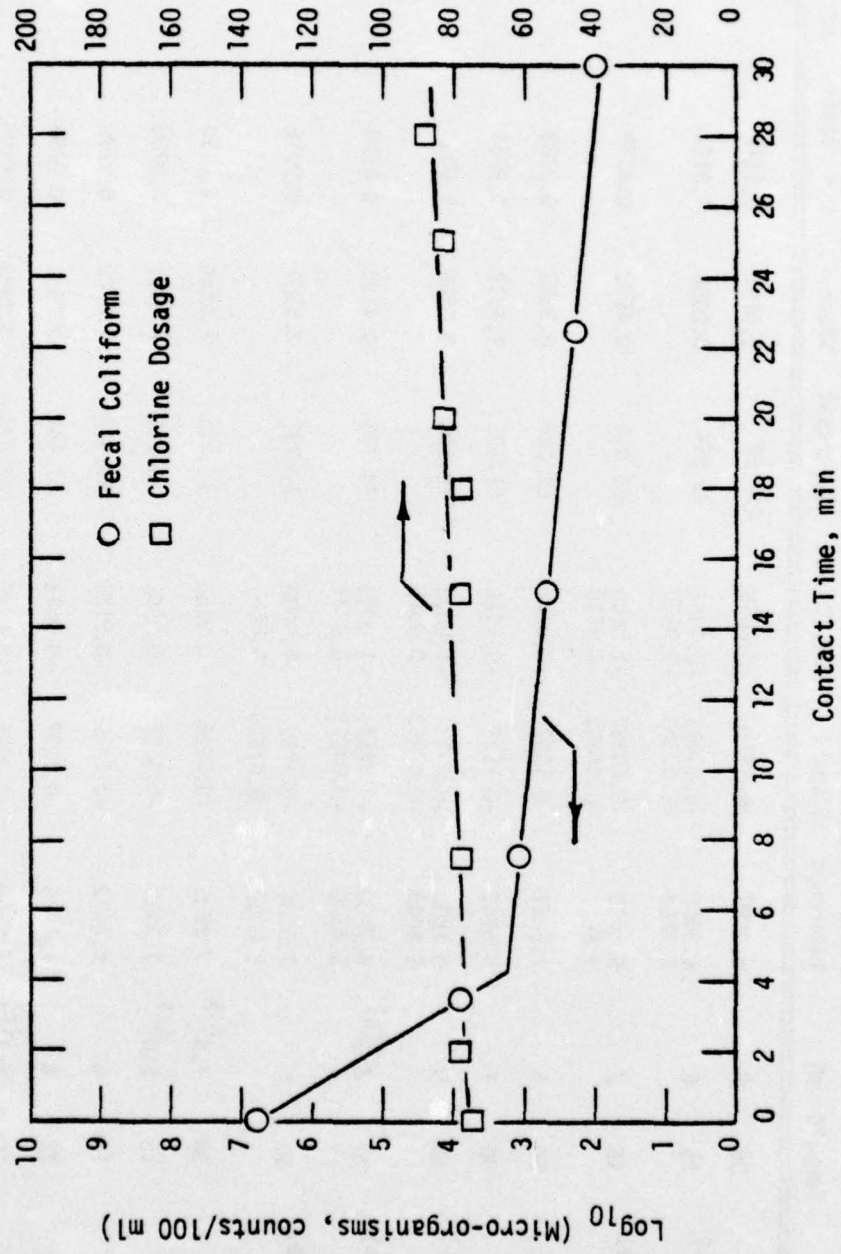


Figure 9: Chlorine Disinfection of Blackwater at 30°C and pH 7

TABLE 3
SUMMARY OF CHLORINATION TEST CONDITIONS AND RESULTS

Run	Temp, °C	pH	Linear Regression of log(F. Coli) vs. Contact Time		Linear Regression of O ₂ Dosage vs. Contact Time		Required Cl ₂ Dosage, mg/l	
			Intercept	L.R. Coeff.	Intercept	L.R. Coeff.		
C-1	30	9	6.2490	-0.07736	-0.8696	227.22	0.9676	330
C-2(b)	15	5	6.2005 2.7852	-0.43083 -0.03340	-0.9964 -0.9933	76.514	0.2056	79.5
C-3(b)	15	7	5.5400 3.8811	-0.60307 -0.07853	-1.0000 -0.9586	65.824	0.4613	75.1
C-4	30	5	7.4251	-0.1632	-0.9812	63.396	0.3483	73.3
C-5	30	7	5.8462	-0.1538	-0.9422	61.195	1.4812	95.3
C-6(b)	15	9	8.1800 5.6000	-0.6923 -0.07253	-1.0000 -0.9316	79.300	0.0000	79.3
C-7(b)	30	7.0(c)	6.7900 3.4300	-0.8257 -0.04853	-1.0000 -0.9982	74.777	0.4106	84.3
C-8(b)	30	5	7.0386 5.0900	-0.1159 0.01200	-1.0000 0.8660	69.735	3.9301	∞
C-9	30	7.6(c)	7.2705	-0.1326	-0.9650	70.215	2.6154	168.3
C-10	15	8.0(c)	7.3478	-0.1522	-0.9902	46.441	1.1901	86.0
C-11	15	6	6.8679	-0.1435	-0.9689	59.012	2.0722	124.9
C-12	30	6	6.8925	-0.1237	-0.9516	67.564	3.1554	184.6
C-13	15	8.4(c)	7.6608	-0.0366	-0.9528	62.673	0.2908	105.1
C-14	30	8.1(c)	7.3930	-0.0516	-0.9260	74.047	1.3863	210.9

a) Dosage required to reduce fecal coliform concentration to 200 colonies/100 ml.
 b) Data for log (F. Coli. Conc.) vs. Contact Time fit by two straight line segments of different slope. Regression values for the line segment applicable at long contact times are listed below those for the line segment applicable to short contact times.
 c) Run conducted at natural pH of waste; no pH adjustment.

three columns of Table 3 give the Run No. and the test conditions. The next three columns give the intercept, slope, and correlation coefficient for the fitted regression line of log (F. Coli. conc.) versus contact time. For runs in which two line segments were required to correlate the data, regression values are listed for both line segments. The correlation coefficients for log (F. Coli. conc.) versus Contact Time ranged from -0.87 to -0.99. (Correlation coefficients of -1.00 were obtained for line segments fitted to only 2 or 3 data points and are not indicative of the overall correlation of the data). The sources of scatter in the data for log (F. Coli. conc.) versus contact time are identical to those cited above for ozonation and are related to problems associated with obtaining accurate samples and analyses for fecal coliform bacteria.

The next three columns of Table 3 give the intercept, slope, and correlation coefficient for the fitted regression line of Chlorine Dosage versus Contact Time. In general the straight line correlation gave a good fit of the data resulting in correlation coefficients ranging from 0.82 to 1.0. At least some of the scatter in the data is related to the slow response of the chlorine monitoring system which resulted in problems maintaining the free available chlorine concentration at a fixed level. However, extrapolation of results using the fitted regression lines should be reasonably accurate: runs for which the correlation coefficient is relatively low (0.82 to 0.90) also have a low slope, and extrapolation to longer contact times has a relatively small effect on the total dosage calculated.

The final column of Table 3 gives the chlorine dosage required to reach a fecal coliform concentration of 200 colonies/100 ml. In most cases, some extrapolation of the straight line relationships was required. The log (F. Coli. conc.) versus Contact Time relationship was extrapolated to determine the contact time at which the fecal coliform concentration reached 200 colonies/100 ml, and the Chlorine Dosage versus Contact Time relationship was extrapolated to determine the chlorine dosage at that same contact time.

The required chlorine dosage from Table 3 is shown as a function of pH in Figure 10. As for the ozonation data, various groups of data points were fit by linear regression to straight-line relationships. The results are shown below.

<u>Data Group</u>	<u>Correlation Coefficient</u>	<u>95% Confidence Interval</u>
All Data (except C-8)	0.403	-0.21 to 0.77
Data at 15°C	-0.138	-0.81 to 0.70
Data at 30°C (except C-8)	0.759	0 to 0.95

For all of the data groups evaluated, the 95% confidence interval includes a correlation coefficient of zero. Therefore, at the 95% confidence level, the data indicate that there is no significant relationship between the chlorine dosage and pH. For the data at 30°C a slight relaxation of the confidence level would result in a statistically significant correlation between the chlorine dosage and pH at this temperature.

A similar analysis was applied to the data for Required Chlorine Dosage vs. Temperature. The correlation coefficient, considering all data except Run C-8, was 0.50 with a 95% confidence interval from -0.07 to 0.82. Thus, at the 95% confidence level, no significant relationship exists between the required chlorine dosage and temperature. However, a slight relaxation of the confidence level would result in a statistically significant positive correlation between the required chlorine dosage and temperature.

As noted previously the composition of the first waste collection changed after some twenty days of testing. In addition to a drop in the pH of the waste, the required ozone dosage increased substantially (see Figure 7, Run 0-10). The required chlorine dosage also increased substantially: Run C-8 (which was conducted on the same day as Run 0-10) was the last chlorination run before the first waste collection was discarded; an infinite (extrapolated) chlorine dosage was required for this run.

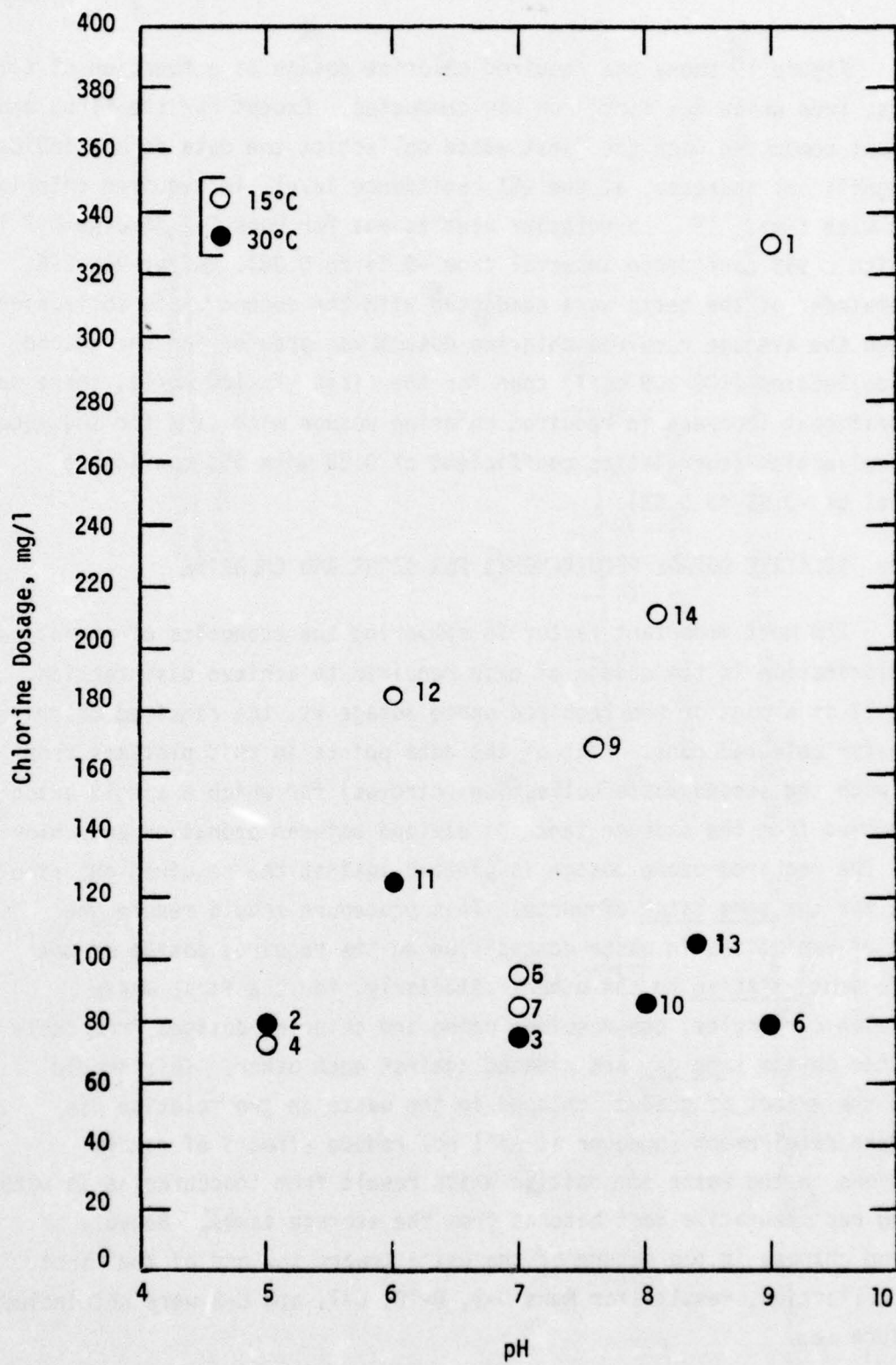


Figure 10: Required Chlorine Dosage vs. pH for Disinfection of Blackwater to 200 Fecal Coliform Colonies per 100 ml.

Figure 11 shows the required chlorine dosage as a function of time, in days, from which the first run was conducted. Except for the first and last runs conducted with the first waste collection the data do not indicate any significant increase, at the 95% confidence level, in required chlorine dosage with time. (The correlation coefficient for Runs C-2 through C-7 is 0.41 with a 95% confidence interval from -0.54 to 0.88). After Run C-8, the remainder of the tests were conducted with the second waste collection. Although the average required chlorine dosage was greater for the second waste collection (100-200 mg/l) than for the first (75-100 mg/l), there was no significant increase in required chlorine dosage with time for the second waste collection (correlation coefficient of 0.23 with 95% confidence interval of -0.65 to 0.83).

D. RELATIVE DOSAGE REQUIREMENTS FOR OZONE AND CHLORINE

The most important factor in comparing the economics of ozonation and chlorination is the dosage of each required to achieve disinfection. Figure 12 is a plot of the required ozone dosage vs. the required chlorine dosage for selected runs. Most of the data points in this plot are from tests with the second waste collection (circles) for which a single batch was removed from the storage tank and divided between ozonation and chlorination. The required ozone dosage is plotted against the required chlorine dosage for the same batch of waste. This procedure should reduce the effect of variations in waste composition on the required dosage of one disinfectant relative to the other. Similarly, for the first waste collection (triangles) the required ozone and chlorine dosages from tests conducted on the same day are plotted against each other. This should reduce the effect of gradual changes in the waste on the relative disinfectant requirement (however it will not reduce effects of random variations in the waste composition which result from inaccuracies in withdrawing representative test batches from the storage tank). Because of observed changes in the nature of the waste toward the end of the first waste collection, results for Runs O-9, O-10, C-7, and C-8 were not included in Figure 12.

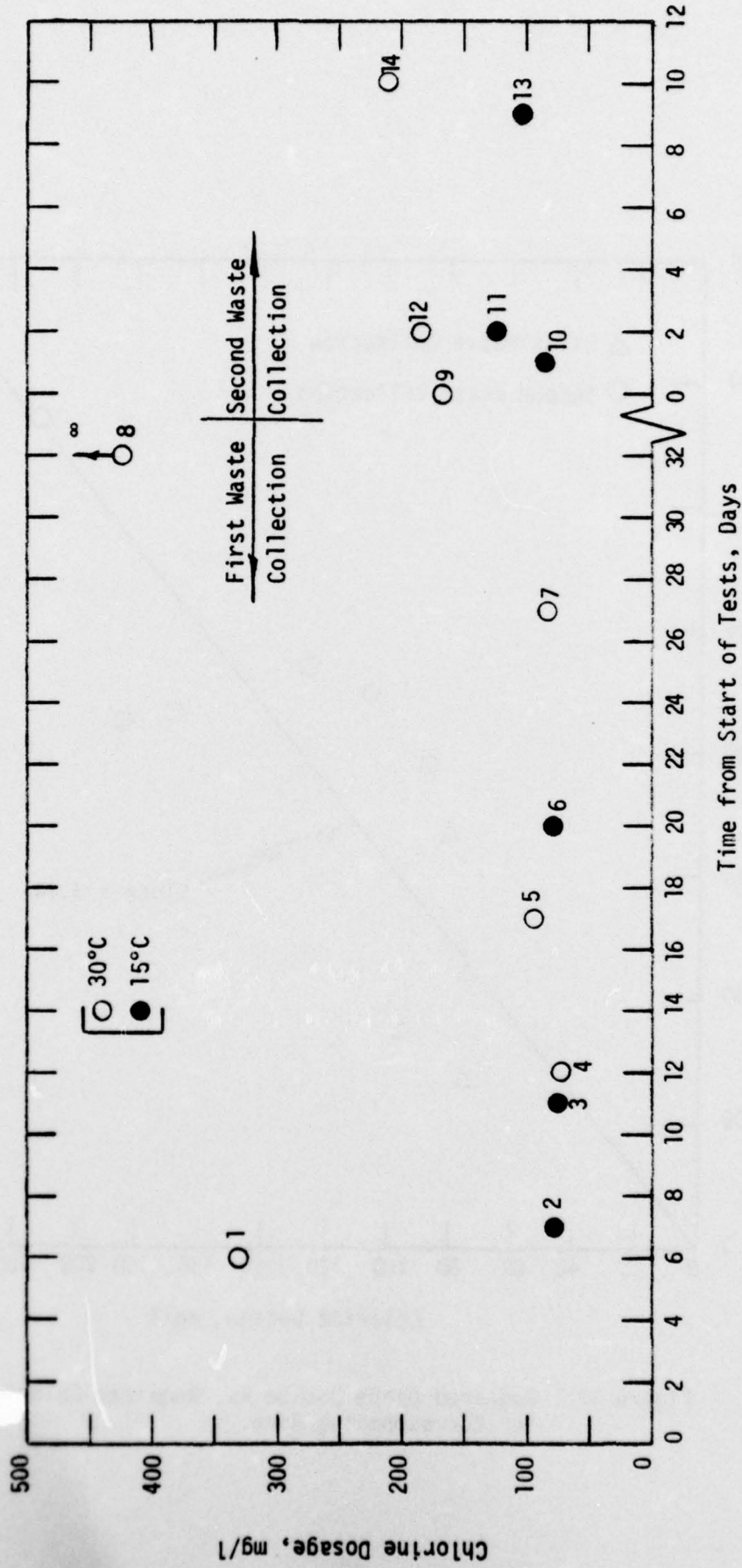


Figure 11: Required Chlorine Dosage vs. Time from Start of Tests for Disinfection of Blackwater to 200 Fecal Coliform Colonies per 100 ml.

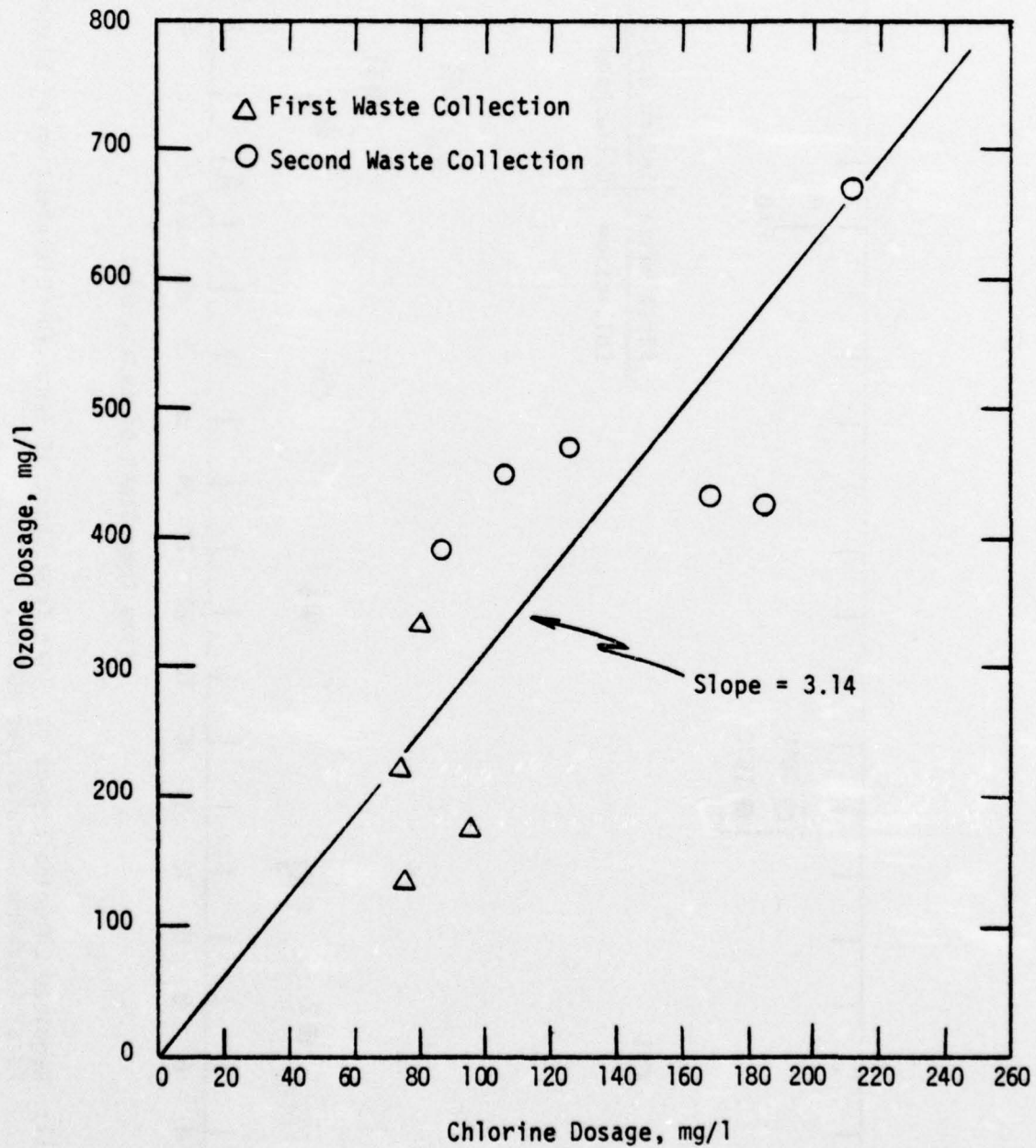


Figure 12: Required Ozone Dosage vs. Required Chlorine Dosage for Corresponding Runs.

The data points of Figure 12 were fit by the method of least squares to a straight line through the origin. The line has a slope of 3.14 indicating that blackwater requires approximately three times more ozone than chlorine for disinfection.

V. DISCUSSION OF RESULTS

A. INFLUENCE OF PROCESS VARIABLES

The details of the mechanisms of disinfection with ozone and chlorine are not well understood. However it is generally believed that disinfection by chlorine results from rapid inactivation of certain enzymes within the cell, ^(5,6) whereas disinfection by ozone results from oxidative degradation of the cell wall or other vital cell constituents. ^(6,7,8) The disinfection mechanism may involve a complex series of physical, chemical, and biochemical reactions which eventually result in the death of the cell. Because of this complexity the influence of process parameters on disinfection is generally described in empirical or phenomenological terms rather than in relation to specific mechanistic steps.

1. Kinetics

The most common kinetic expression for disinfection reactions is Chick's Law ⁽⁹⁾:

$$-\frac{dN}{dt} = kN \quad (1)$$

or in integrated form:

$$\log \frac{N}{N_0} = -\frac{kt}{2.303} \quad (2)$$

where

N = No. of microorganisms surviving at any given time, t,

N₀ = No. of microorganisms at time zero,

K = Rate constant; dependent on the microorganisms, the disinfectant and its concentration, temperature, pH, etc.

All of the ozonation data and most of the chlorination data indicate a linear decrease of log (F. Coli. conc.) with time. (For the ozonation data log [F. Coli. conc.] was plotted against ozone dosage, but since the dose rate was approximately constant during each run, the dosage and time

can be interchanged as the independent variable in the correlation). Thus, for the most part, the experimental results follow Chick's Law (equation [2]), and indicate that the rate of kill is directly proportional to the number of microorganisms present at any time.

Some of the chlorination data indicate a rapid initial decline in bacteria concentration followed by a more gradual decline. This is probably the result of the test procedures in which a large dose of hypochlorite was added initially followed by smaller doses added as required to maintain the desired residual of free available chlorine. The initial rapid decline would then correspond to a more rapid disinfection rate obtained at a higher concentration of hypochlorite (higher value of k in equations [1] and [2]).

2. Effect of Process Parameters on Disinfection Kinetics

As would be expected based on the law of mass action, the rate of disinfection increases as the concentration of disinfectant increases. The rate also increases with temperature as would be expected from the Arrhenius-type rate expressions characteristic of chemical reactions. UV irradiation can increase the rate of disinfection⁽¹⁰⁾ by acting as a catalyst either to activate the microorganism toward ozone attack or to promote the decomposition of ozone to free radicals (e.g. $\cdot\text{OH}$) which may be more reactive than the parent molecule.

The pH can have a substantial effect on the rate of disinfection with chlorine because of the ionization equilibrium of hypochlorous acid:



At high pH the equilibrium is shifted toward the hypochlorite ion. Since HOCl is a more powerful disinfectant than OCl^- , the rate of chlorine disinfection decreases with increasing pH.

The pH can also affect the rate of disinfection with ozone. Hydroxide ion promotes the decomposition of ozone to free radicals. This

may result in either an increase or decrease in the disinfection rate depending on the relative reactivities of ozone and free radical decomposition products toward the microorganisms.

3. Effect of Process Parameters on Required Dosage

The overall kinetics of the disinfection reaction determines the detention time required for treatment and thereby the volume and capital cost of the contacting chamber. However, the effects of disinfection rate on the overall economics are generally minor. Of more importance in determining the economics is the dosage of disinfectant required to reduce the microorganisms to the specified level; hence the experimental program focused primarily on the determination of dosage requirements.

Changes in process parameters such as temperature, pH, and UV irradiation can result in a change in the mechanisms of disinfection which can, in turn, affect the dosage requirement. In addition, these same process parameters can have a large effect on the rate of reaction of the disinfectant with non-biological dissolved species such as organics and ammonia. The required dosage will increase if the change in a process parameter promotes these non-biological reactions relative to the disinfection reactions.

For ozonation none of the correlations between the required ozone dosage and the level of various process parameters (temperature, pH, UV irradiation) was significant at the 95% confidence level. This indicates that the variability in the data was primarily the result of something other than these parameters. If temperature, pH, and UV effects do occur, the effects are small relative to the variability of the data.

For chlorination the required dosage appeared to increase with temperature and pH (at 30°C) but the correlations were not quite significant at the 95% confidence level. An increase in required dosage with pH could be explained in terms of the hypochlorous acid ionization equilibrium mentioned previously. Bacteria exhibit surface charges analogous to amphoteric amino acids which form anions in basic solution, cations in acidic solution, and neutral molecules at some intermediate pH. In basic

solution, the anionic charge repels OCl^- , the predominant disinfectant species; whereas in acidic solution, where HOCl predominates, the disinfectant rapidly permeates the cell membrane resulting in a more efficient utilization of the free available chlorine. The close relationship between disinfection efficiency and the pH dependence of the HOCl ionization equilibrium has been demonstrated previously⁽¹¹⁾. It is of interest to note that no pH effect was observed at a temperature of 15°C , nor was the pH effect significant when data at both 15°C and 30°C were considered.

In addition to temperature, pH, and UV irradiation the required dosage can be affected by the characteristics of the waste being treated. For the most part, gradual changes in the waste during collection/storage did not appear to be significant. At the 95% confidence level there was no significant change in initial fecal coliform concentration over the duration of the tests. In addition the required disinfectant dosages for the separate waste collections did not increase significantly during the test period except perhaps for the ozone dosage for the first waste collection (Figure 7). The most probable explanation of this increase in required ozone dosage is that the concentration of easily ozonated dissolved species increased during the first waste collection either as the result of chemical changes in the waste or the addition of fresh waste having a higher content of easily ozonated dissolved species. A similar increase in required chlorine dosage did not occur during the first waste collection since chlorine is generally much less reactive than ozone toward dissolved species. The very high ozone and chlorine dosages required for the last run before the first waste collection was discarded is probably the result of changes in the waste, but the nature of these changes remains open to speculation.

Although some of the variability in the ozonation data for the first waste collection may be explained by a gradual change in the non-bacterial ozone demand, this does not account for all the variability. There appear to be substantial run-to-run or random variations which are unrelated to the variables discussed above. These variations could arise from run-to-run differences in the waste being treated or from experimental error.

Because of the high suspended solids concentration of black-water it is difficult to withdraw a representative sample from the waste storage tank as pointed out in Section IV-A. This resulted in significant run-to-run variations in the waste being treated. These short-term variations, such as differences in the initial bacterial concentrations and differences in the amount of bacteria occluded in suspended matter, can account for at least some of the variability in the data.

In addition there is room for significant effects resulting from experimental error. Although reasonably good correlation coefficients were obtained for the raw data (log [F. Coli. Conc.] vs. Ozone Dosage or Chlorine Contact Time), only six data points were obtained for each run. With so few data points the 95% confidence interval would allow a substantial variation in the slope of the correlation. Thus the required disinfectant dosage determined from the regression analysis is subject to considerable uncertainty, particularly when extrapolation was required to reach the specified level of 200 calories/100 ml.

B. ECONOMICS

It is difficult to make an accurate assessment of the economics because of certain undefined factors associated with this particular application. Nevertheless an estimate of the operating cost was made on the basis of a set of seemingly reasonable assumptions. The assumptions and calculations are given in Table 4. The calculated cost for ozonation is 1.8 cents per man-day; while the calculated cost for chlorination is 0.58 cents per man-day. The higher cost for ozonation is a direct result of the higher required ozone dosage. If the required dosages of ozone and chlorine were the same, the operating costs would have been nearly identical.

It is apparent that the fixed capital cost for an ozonation system will be significantly greater than for a chlorination system because of the need for an air compressor, dryer, and ozone generator. The capital cost for an ozone generator which produces one pound per day of ozone from air is approximately \$5000⁽¹²⁾ (including compressor and air dryer). Based on the assumptions of Table 4, a generator of this size would be sufficient

TABLE 4
 ASSUMPTIONS AND CALCULATIONS OF OPERATING COSTS FOR OZONATION
 AND CHLORINATION OF BLACKWATER

Assumptions:

1. Each man produces 6 gal of blackwater per day (3 gal/flush x 2 flushes/day).
2. A chlorine dosage of 240 mg/l and an ozone dosage of 750 mg/l (see Figure 12) will insure disinfection to the desired level.
3. The on-board cost for a 15% solution of NaOCl is \$0.64 per gal of solution (current local price for 55 gal drums).
4. The on-board cost for electrical power is \$0.04/kwh.
5. The power requirement for ozone generation including air compressor and dryer is 12 kwh/lb ozone⁽¹³⁾.
6. Operating labor and maintenance are negligible for both ozonation and chlorination.

Basis: One man-day

Ozonation Operating Cost:

$$\frac{6 \text{ gal}}{1} \times \frac{3.785 \text{ l}}{1 \text{ gal}} \times \frac{750 \text{ mg O}_3}{1 \text{ liter}} \times \frac{\text{g}}{1000 \text{ mg}} \times \frac{1 \text{ lb}}{454 \text{ g}} \times \frac{12 \text{ kwh}}{1 \text{ lb}} \times \frac{\$0.04}{1 \text{ kwh}} = \$0.018$$

Chlorination Operating Cost:

$$\frac{6 \text{ gal}}{1} \times \frac{3.785 \text{ l}}{\text{gal}} \times \frac{240 \text{ mg Cl}_2}{1} \times \frac{\text{g}}{1000 \text{ mg}} \times \frac{74.5 \text{ g NaOCl}}{71 \text{ g Cl}_2} \times \frac{\text{g soln}}{0.15 \text{ g}}$$

$$\times \frac{\text{cc soln}}{1.12 \text{ g}} \times \frac{1 \text{ gal}}{3,785 \text{ cc}} \times \frac{\$0.64}{\text{gal}} = \$0.0058$$

for a crew of about 25 men. Considering the cost for contactors and the cost for installation, it is estimated that the cost of an unsophisticated ozonation system for a 25-man crew would be about \$8,000 compared to about \$3,000 for chlorination.

Although both the capital and operating costs for ozonation are about three times as great as for chlorination, the absolute costs for ozonation do not appear excessive relative to other ship-board capital and operating expenses. For example the daily operating cost of ozonation for a 25-man crew is only 45 cents, or only 30 cents more than chlorination per day. This would seem to be a relatively small penalty to pay for a reduction in the amount of chlorinated hydrocarbons produced and for an increase in the inactivation of viruses. However the trade-off between costs and control of hazardous substances in the discharge requires subjective decisions beyond the intended scope of this program.

VI. CONCLUSIONS

The results of this study lead to the following conclusions.

1. Both ozone and chlorine are effective disinfectants for blackwater.
2. None of the process parameters investigated (temperature, pH, UV irradiation) had a significant effect on the ozone or chlorine dosage required for disinfection to a level of 200 fecal coliform colonies per 100 ml. (However the correlations between required chlorine dosage and temperature, and required chlorine dosage and pH at 30°C were significant at a confidence level slightly below 95%).
3. Most of the variability in the data appeared to result from problems in obtaining a reproducible waste for all tests and from other sources of experimental error.
4. The required dosage of ozone was approximately three times as great as the required dosage of chlorine.
5. Both the estimated capital and operating costs for disinfection of blackwater are about three times as great for ozonation as for chlorination.
6. The additional investment and operating cost for an ozonation system do not appear to be excessive relative to other ship-board expenses. However the final trade-off analysis between the advantages of ozone treatment and its cost disadvantage require the application of subjective criteria beyond the scope of this program.

VII. RECOMMENDATIONS

The findings of this program should be reviewed by USAMERDC to determine if the increased cost for ozonation of blackwater is justified by the reduction of hazardous substances returned to the environment. However, before additional development work on either ozonation or chlorination is conducted, alternative process options should be considered.

One of the disadvantages of direct disinfection is that it will not meet the final proposed standard (1980) for suspended solids (150 mg/l). This standard implies that filtration will have to be used in addition to disinfection. During this program ultrafiltration (UF) was evaluated as a technique for treating blackwater. The results of this evaluation are presented and discussed in Appendix D. It is concluded that UF treatment of blackwater appears to be highly promising.

One of the unique advantages of UF relative to conventional filtration is that the UF membranes remove much of the bacteria along with other suspended solids. Removal efficiencies in excess of 99.999% were measured for fecal coliform bacteria. Therefore, one treatment process that would appear promising is ultrafiltration of blackwater followed by disinfection of the ultrafiltrate (permeate) prior to discharge. Disinfection could be achieved by chlorination, ozonation, or UV irradiation, but regardless of the disinfectant, the costs and reliability requirements for disinfection will be substantially reduced since UF removes almost all of the bacteria.

Evaluation and development of a combined UF-disinfection system is recommended. If successfully developed, such a system would meet the proposed final standards (1980). Development of a direct ozonation system as a replacement for chlorination to meet the interim standards (1977) should be questioned in light of the limited environmental benefits that would accrue prior to deployment of systems that can meet the final proposed standards.

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APPENDIX A
DATA REDUCTION

This appendix describes the procedures and calculations used in reducing the data. The procedures for ozonation and chlorination are described separately using Runs 0-1 and C-1 as illustrative examples.

Ozonation

The tabulated data for Run 0-1 is presented in Table A-1. Column 1 gives the time (independent variable) at which the other values of Table A-1 were obtained. Column 2 gives the flow rate of the ozone stream in CFH measured at ambient temperature and pressure. Column 3 gives the difference in ozone concentration of the feed stream and off-gas from the contactor. In all cases the concentration of ozone in the off-gas was negligible; so the values of Column 3 are equivalent to the feed concentration of ozone. Column 4 gives the time interval for which discrete dosages are to be calculated. These values are obtained from Column 1 by subtracting the previous entry from the given entry. Column 5 gives the ozone consumed during the time interval of Column 4. Values were calculated using the following equation.

$$\begin{aligned} \Delta \text{ Ozone Consumed} &= F \frac{\text{ft}^3}{\text{hr}} \times \frac{273}{298} \frac{\text{SCF}}{\text{ft}^3} \times \frac{28.32 \text{SL}}{\text{SCF}} \times \frac{\text{mole}}{22.4 \text{SL}} \times \frac{32 \text{g}}{\text{mole}} \times \frac{\Delta \% \text{O}_3}{100} \\ &\times \frac{1000 \text{mg}}{\text{g}} \times \frac{1 \text{hr}}{60 \text{min}} \times \Delta t \text{ min} \\ &= 6.17 F (\Delta\%) (\Delta t) \text{ mg O}_3 \text{ Consumed} \end{aligned}$$

Column 6 gives the volume of waste being treated during the time interval of Column 4. The volume changed because of the removal of liquid samples for bacteria analysis. (In later tests much smaller volumes were removed). Column 7 gives the ozone dosage consumed over the time interval; these values were calculated by dividing the entries of Column 5 by the corresponding entries of Column 6. Column 8 gives the cumulative ozone dosage consumed, determined by adding the entries of Column 7. Columns 9 and 10 give the logarithms of fecal coliform concentration (in colonies per 100 ml) and total-plate-count concentration (in counts per ml), respectively. The

TABLE A-1
DATA FOR OZONATION RUN 0-1

1	2	3	4	5	6	7	8	9	10
Time, min	Ozone Flow, CFH	$\Delta\%O_3$, %	Δ Time, min	Δ Ozone Consumed, mg	Waste Volume,* liters	Δ Dosage Consumed, mg/l	Cum. Dosage Consumed, mg/l	Log F. Coli Conc.	Log T. Plate Conc.
0	2.0	1.0	--	--	14.5*	--	0	6.89	9.30
15	2.0	1.0	15	185	13.5	13.7	13.7	6.22	8.00
30	2.0	1.0	15	185	12.5	14.8	28.5	4.95	7.88
60	2.0	1.0	30	370	11.5	32.2	60.7	4.81	7.30
90	2.0	1.1	30	407	10.5	38.8	99.5	3.58	7.04
120	2.0	1.1	30	407	9.5	42.8	142.3	1.90	4.00

*Volume recorded before removal of liquid sample for analysis

"raw data" consist of plots of Columns 9 and 10 against Column 8.

Chlorination

The tabulated data for RunC-1 are presented in Table A-2. Column 1 gives the time (independent variable) at which the other entries in Table A-2 were obtained. Column 2 gives the volume of sodium hypochlorite solution added. The concentration of free available chlorine (as chlorine) in the NaOCl solution was determined by Standard Methods⁽²⁾ assays 114D and 115 to be 31 g Cl₂ per liter. The chlorine concentration was checked several times during the tests, and no substantial change was observed. Column 3 gives the volume of waste in the contactor. A flow of 100 cc/min was discarded from the chlorine monitor and one-liter liquid samples were withdrawn for analysis. (During later runs the sample volume was substantially reduced.) The volumes shown were the measured volume before withdrawal of the liquid sample. Column 4 gives the dosage over the time interval indicated in Column 1. For example the dosage over the interval from 7.5 to 13.5 minutes is: 5 ml NaOCl solution (added at 7.5 min), times 31 mg Cl₂ per ml solution, divided by 11.65 liters of waste = 13.3 mg/l. Column 5 gives the cumulative chlorine dosage determined by adding appropriate entries of Column 4. Columns 6 and 7 give the logarithms of fecal coliform concentration (in colonies per 100 ml) and total bacteria concentration (in counts per ml), respectively. The "raw data" consist of plots of Columns 5, 6, and 7 against Column 1.

TABLE A-2
DATA FOR CHLORINATION RUN C-1

1 Time, min	2 Vol. NaOCl Soln. Added, ml	3 Waste Volume, liters	4 Δ Dosage Added, mg/l	5 Cum. Dosage Added mg/l	6 Log F. Coli Conc.	7 Log T. Plate Conc.
0	107	15			6.26	7.95
2.0	0	14.8	224	224		
3.25	5	14.675	0	224	6.28	7.63
7.5	5	13.25	11.7	236	5.08	6.76
13.5	2.5	11.65	13.3	249		
15	2.5	11.50	6.7	256	5.04	6.67
22.5	2.0	9.75	7.9	264	5.32	6.70
26	1.0	8.40	7.4	271		
30	0	7.00	4.4	275	3.46	4.56

APPENDIX B
DATA FOR OZONE DISINFECTION OF BLACKWATER

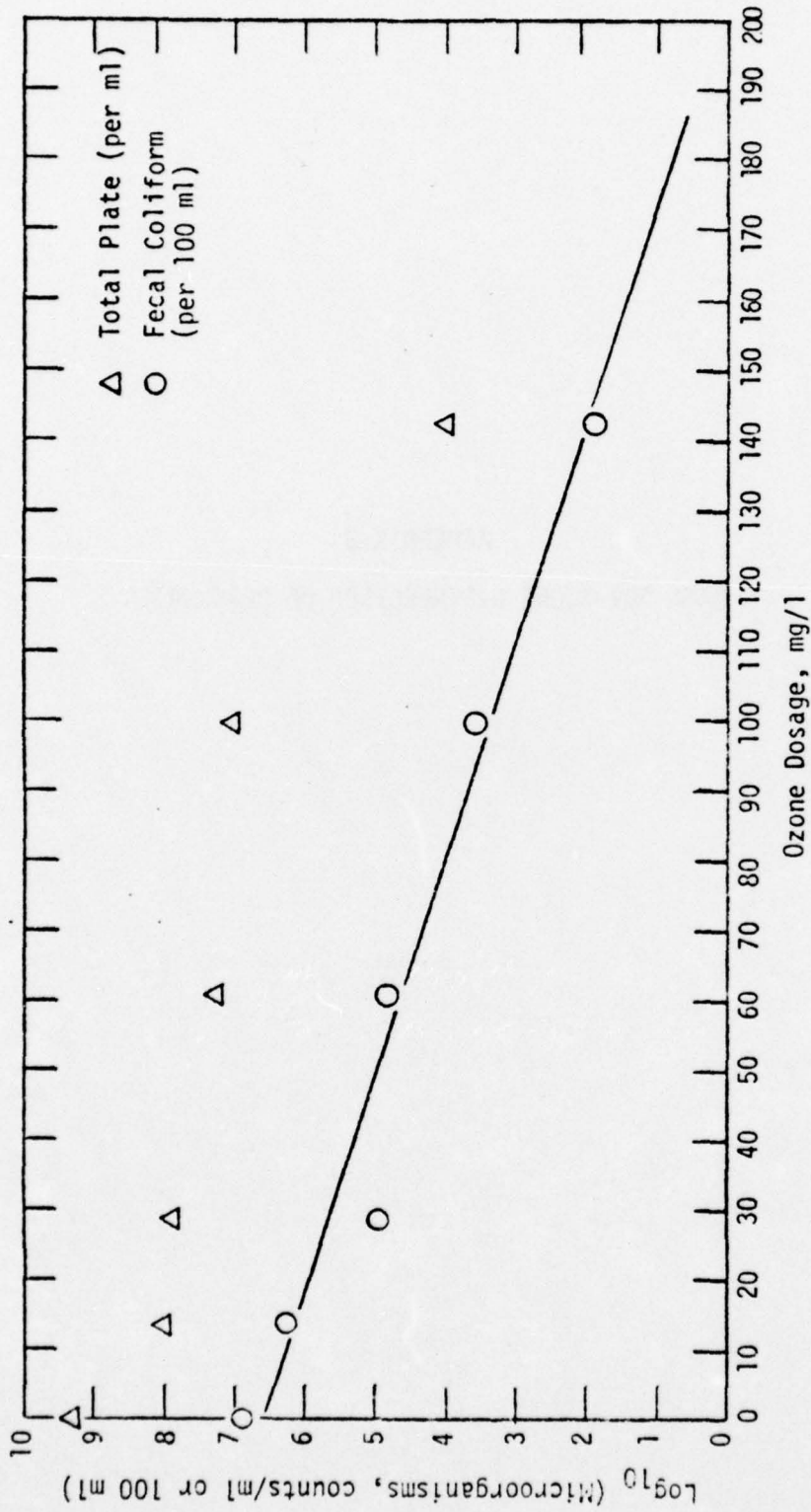


Figure B-1: Ozone Disinfection of Blackwater at 30°C, pH 9, and no UV; Run 0-1

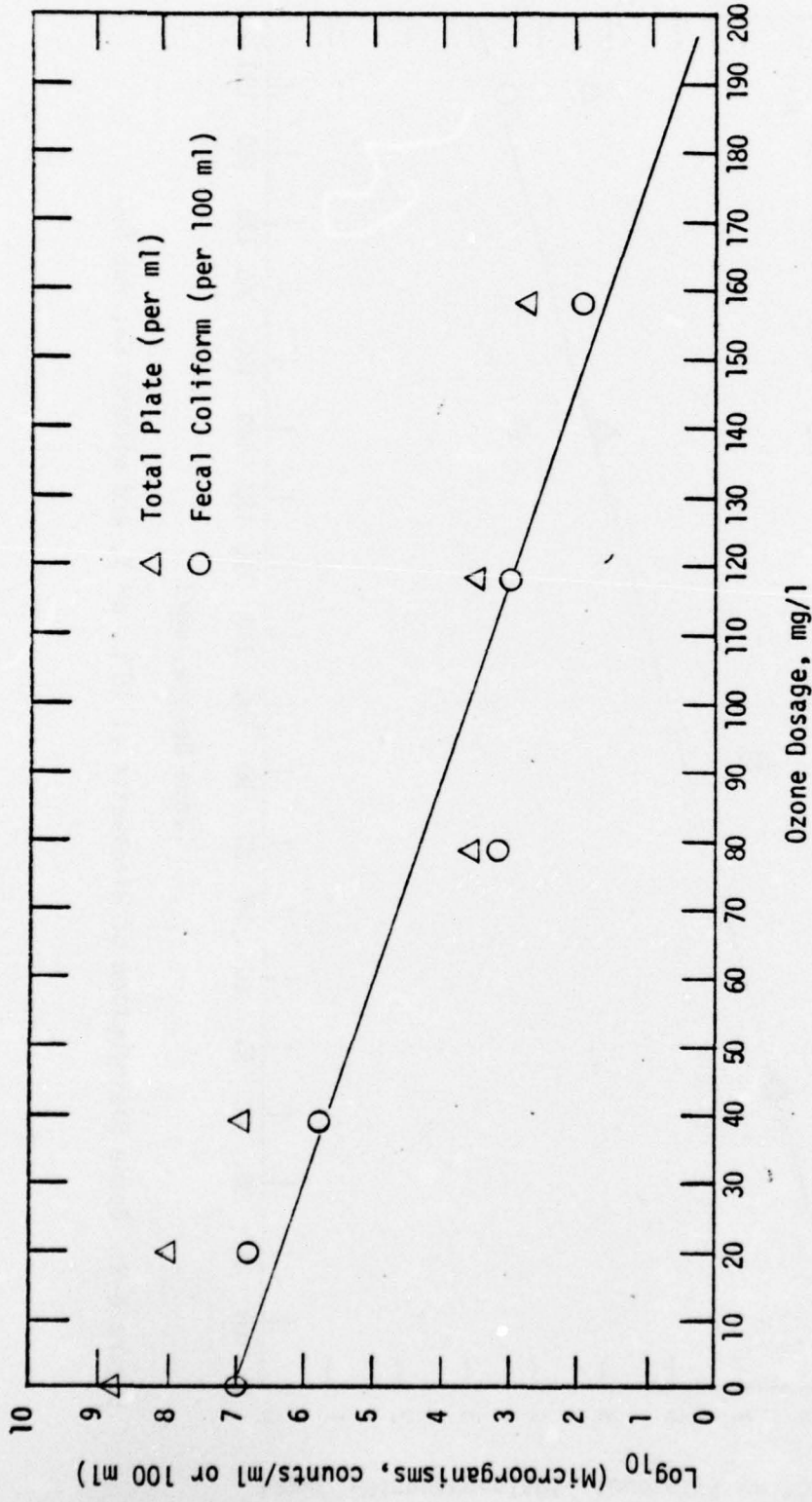


Figure B-2: Ozone Disinfection of Blackwater at 15°C, pH 5, and without UV; Run 0-2

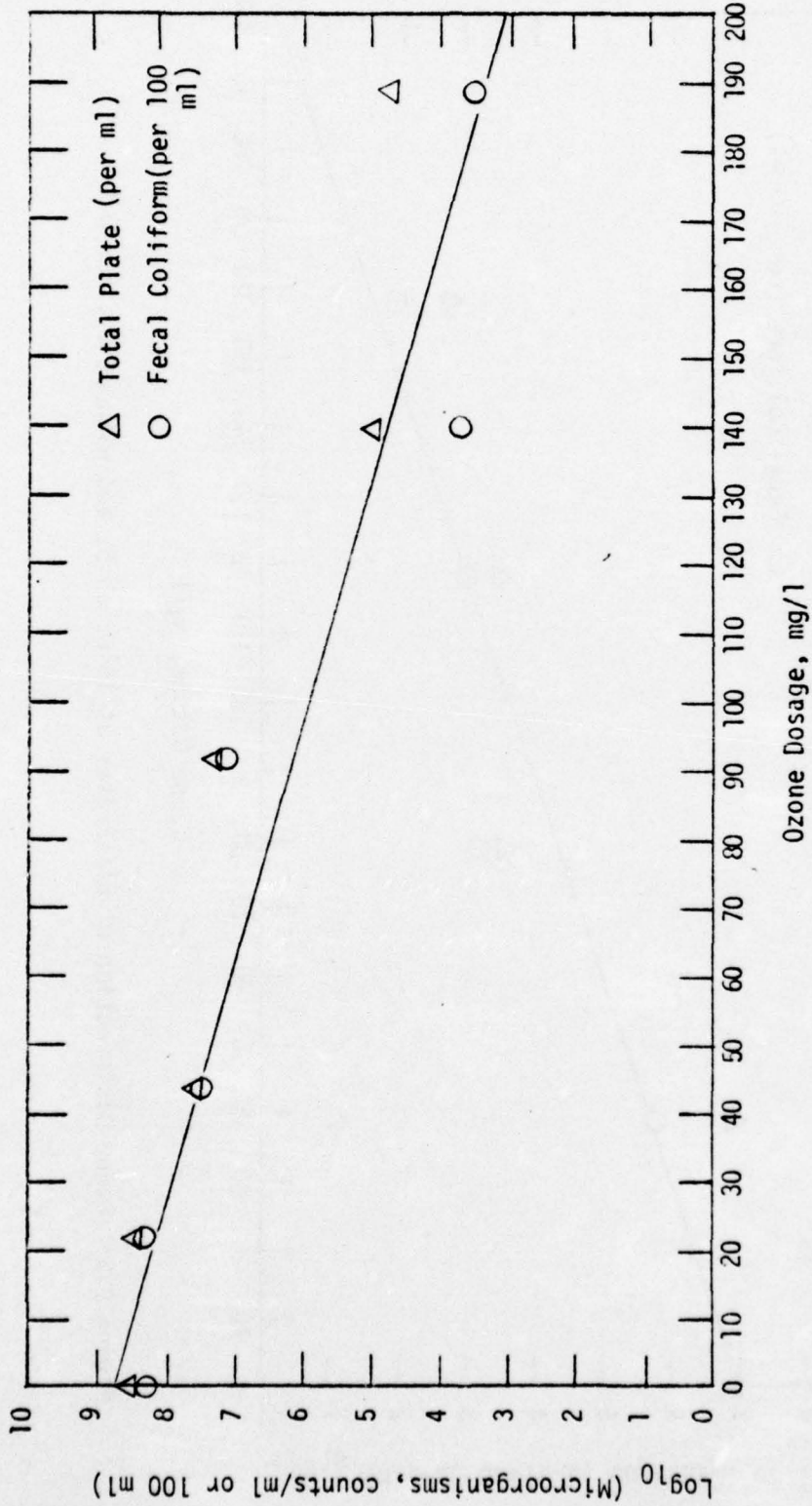


Figure B-3: Ozone Disinfection of Blackwater at 15°C, pH 7, and without UV; Run 0-3

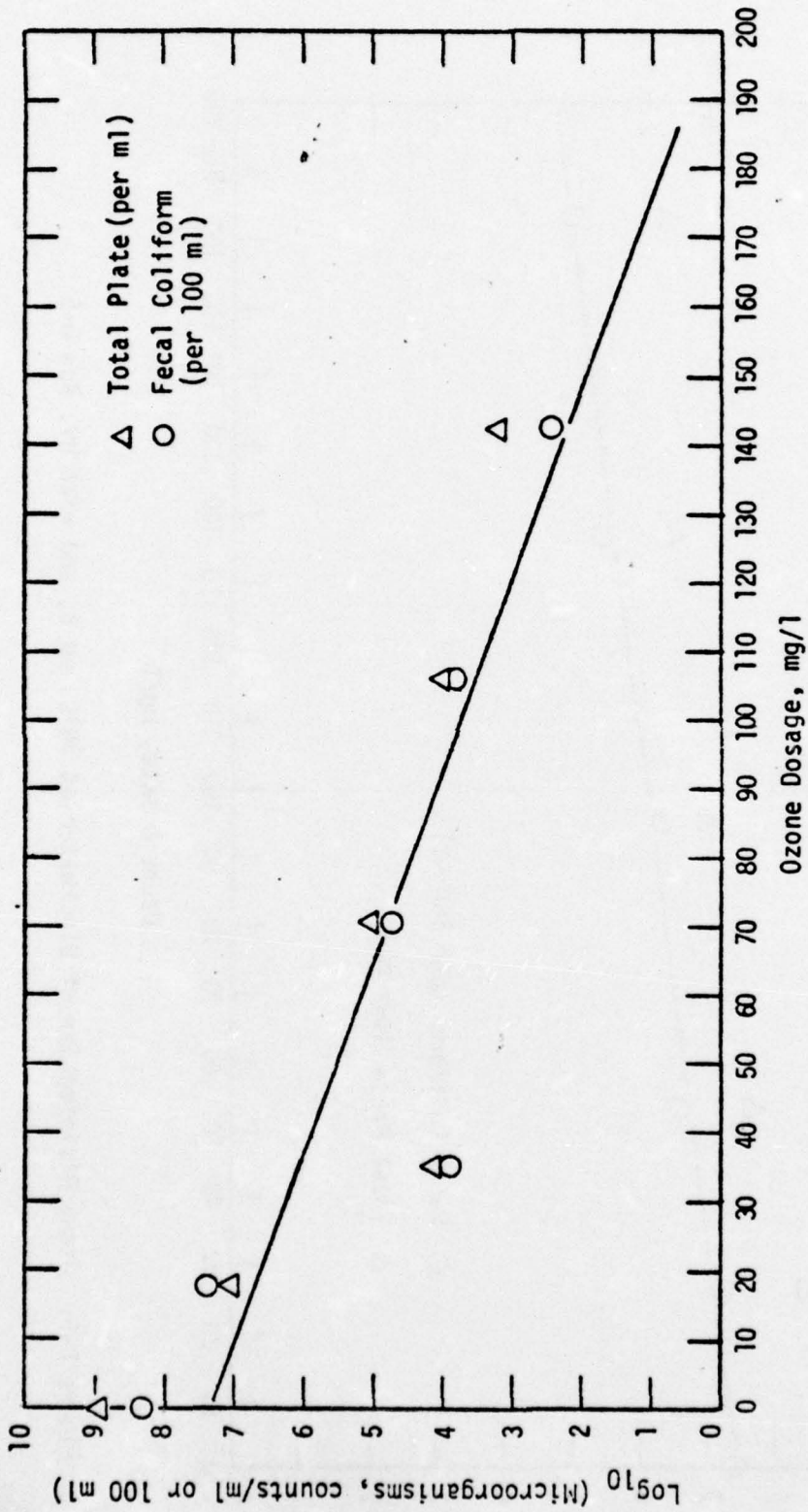


Figure B-4: Ozone Disinfection of Blackwater at 30°C, pH 5, and No UV; Run 0-4

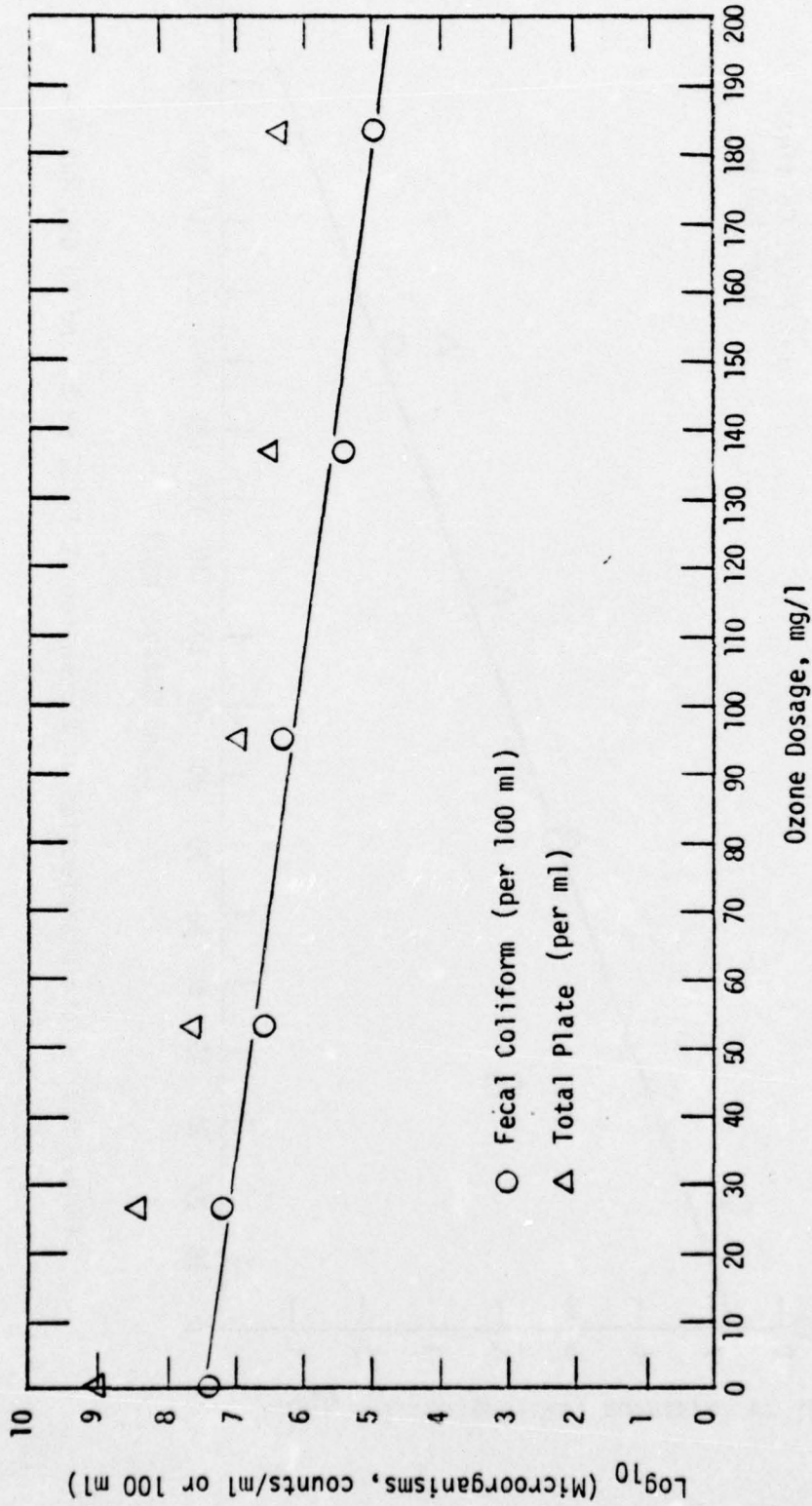


Figure B-5: Ozone Disinfection of Blackwater at 30°C, pH 5, and with UV; Run 0-5

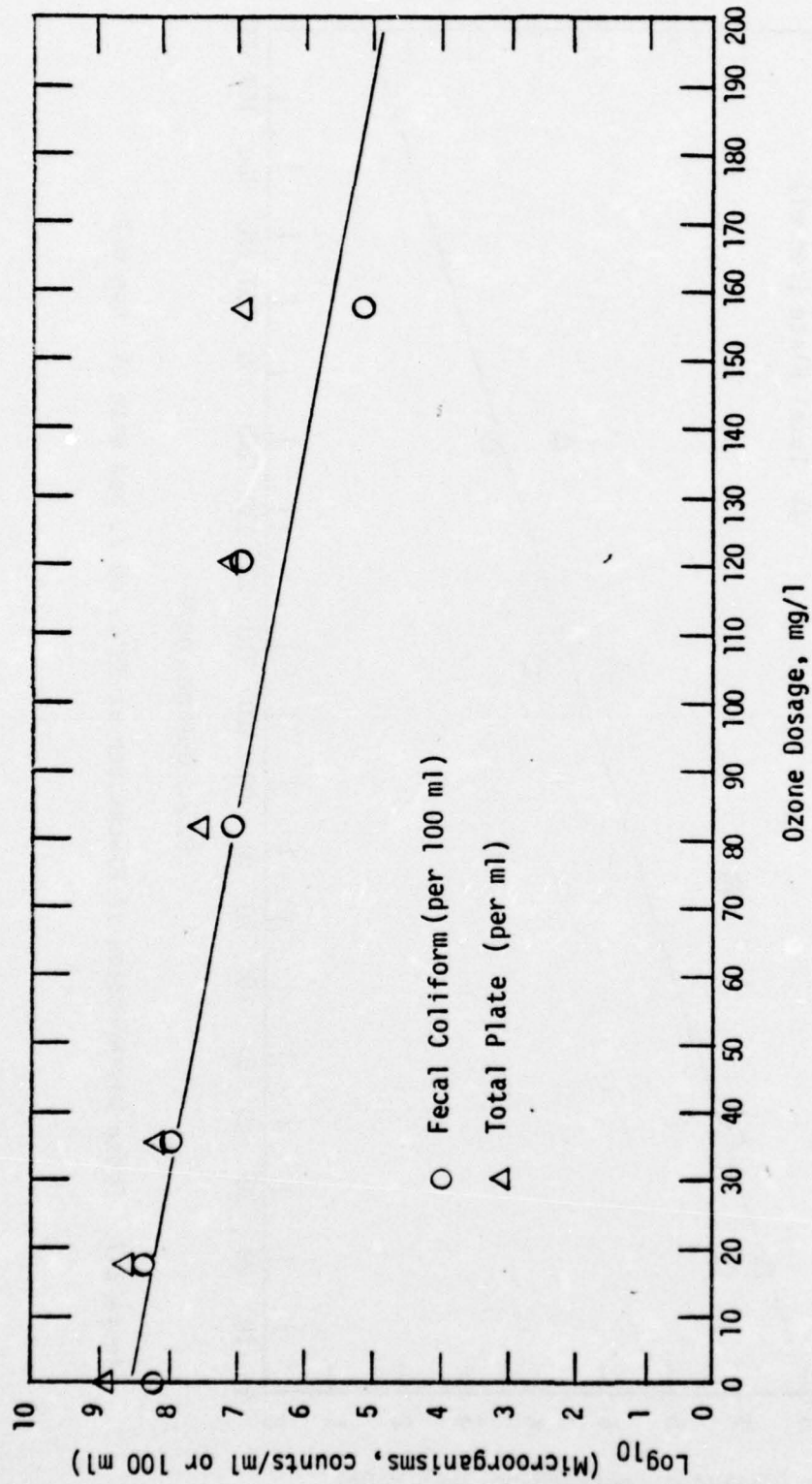


Figure B-6: Ozone Disinfection of Blackwater at 30°C, pH 7, and without UV; Run 0-6

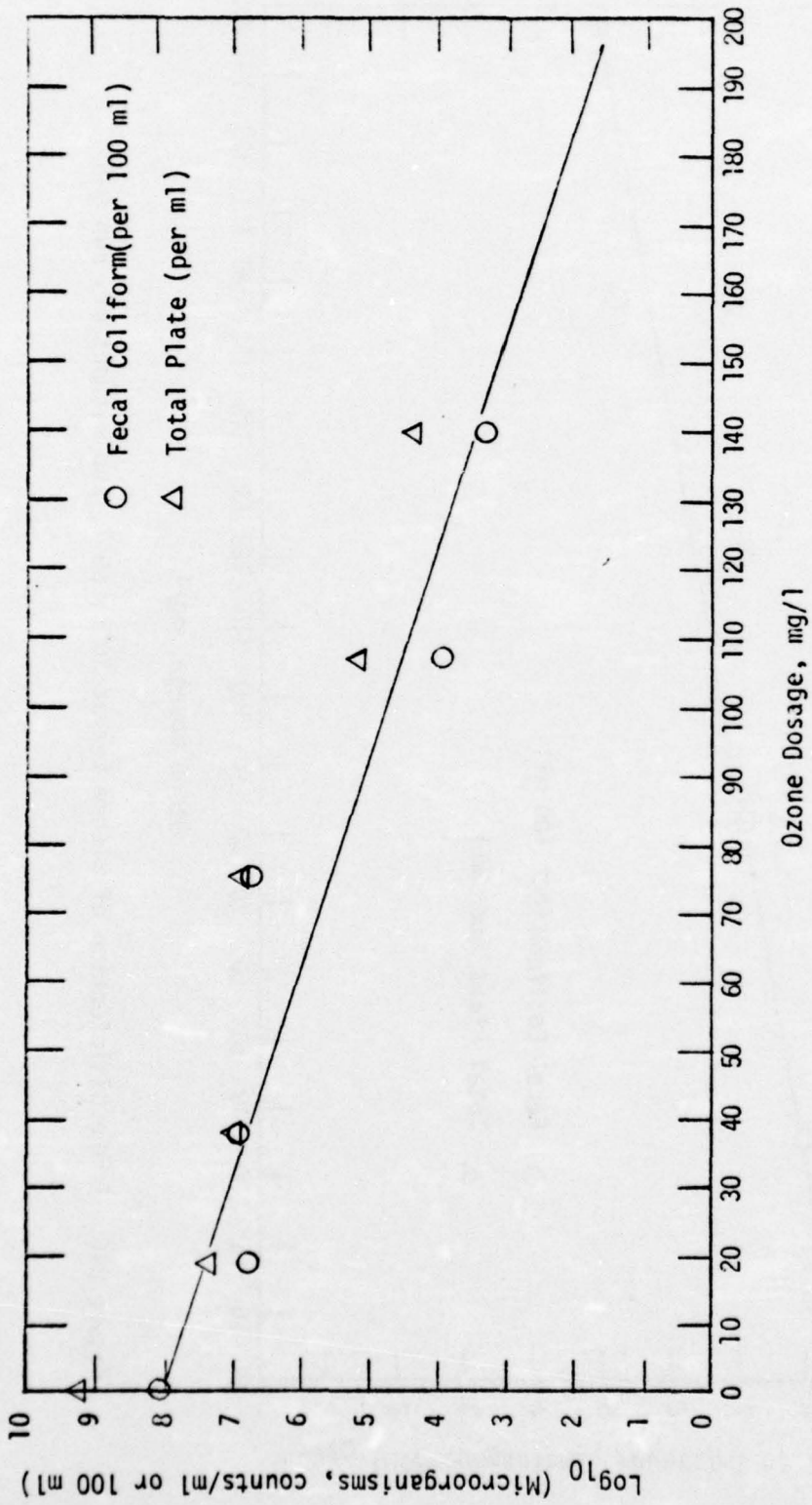


Figure B-7: Ozone Disinfection of Blackwater at 30°C, pH 7, and with UV; Run 0-7

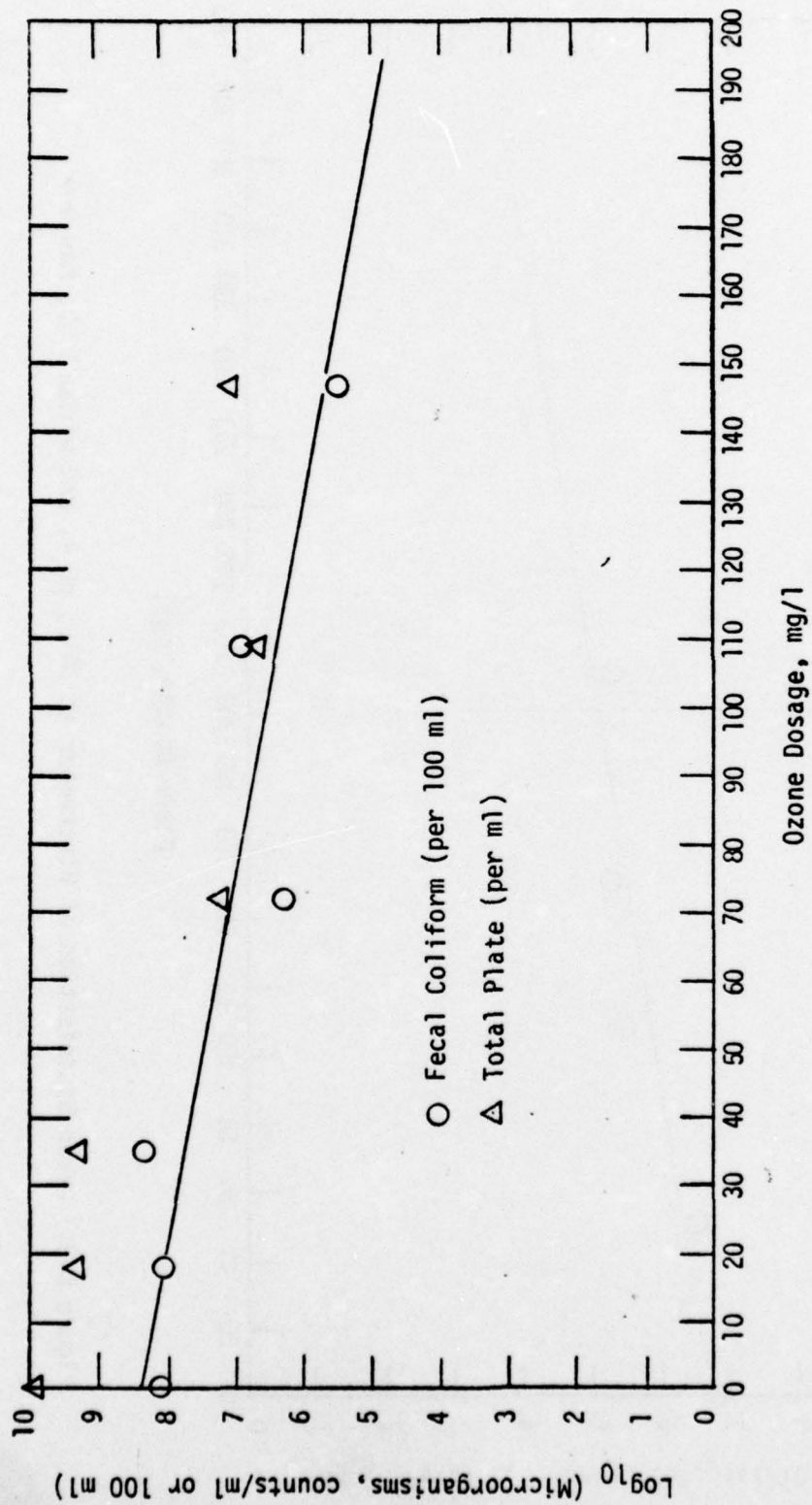


Figure B-8: Ozone Disinfection of Blackwater at 15°C, pH 9, and without UV; Run 0-8

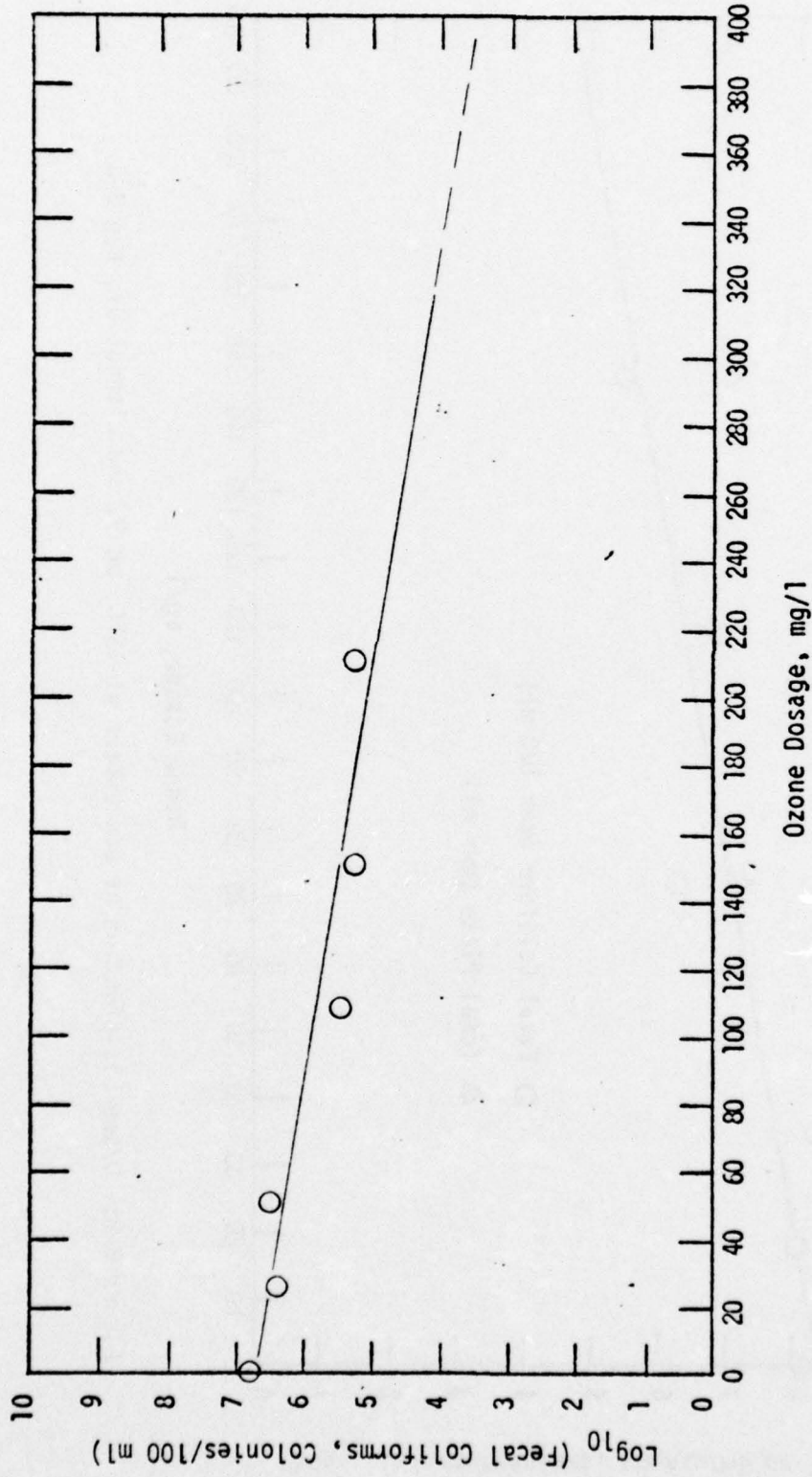


Figure B-9: Ozone Disinfection of Blackwater at 30°C, pH 7, and without UV; Run 0-9

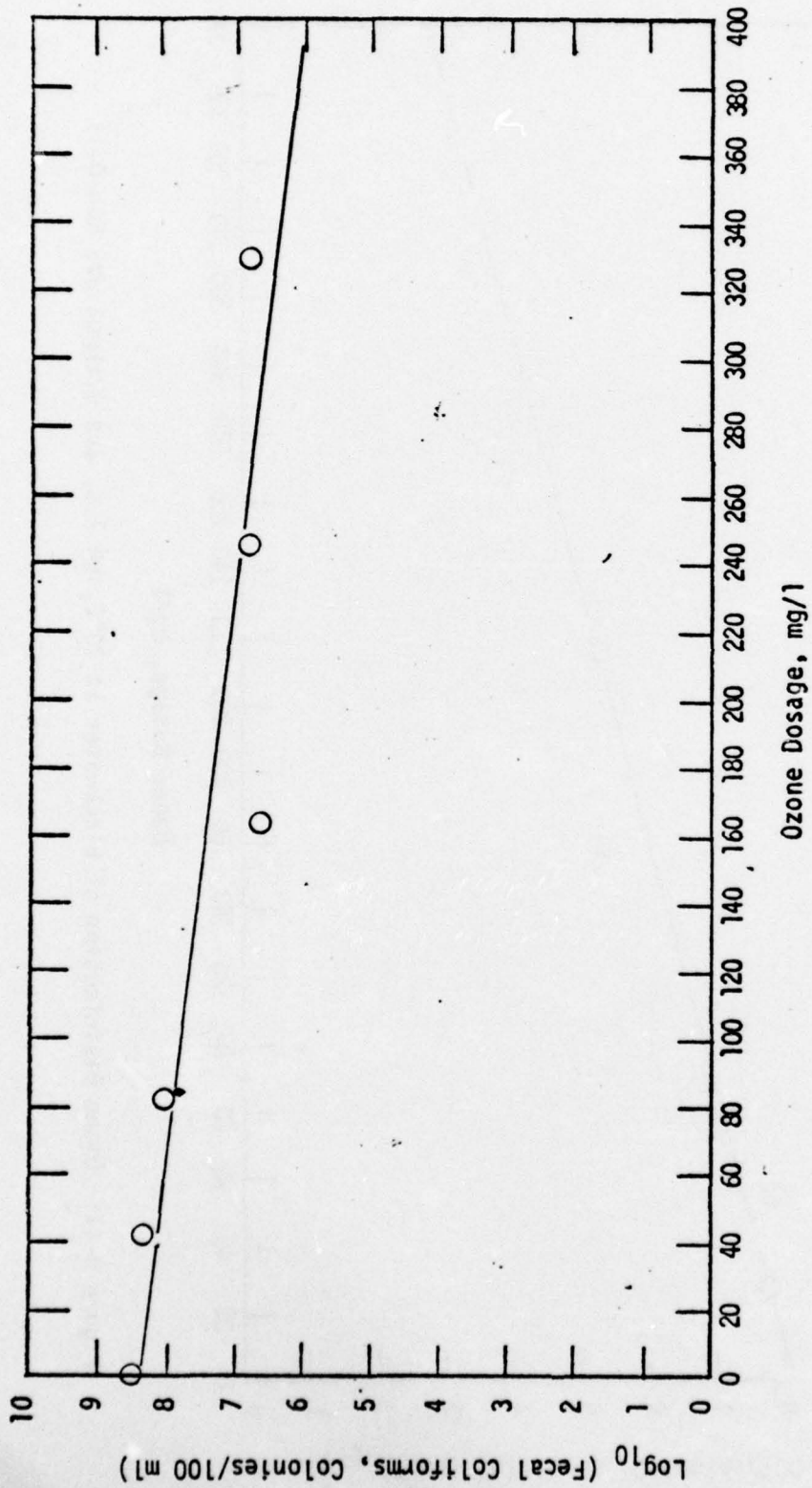


Figure B-10: Ozone Disinfection of Blackwater at 30°C, pH 7, and without UV; Run 0-10

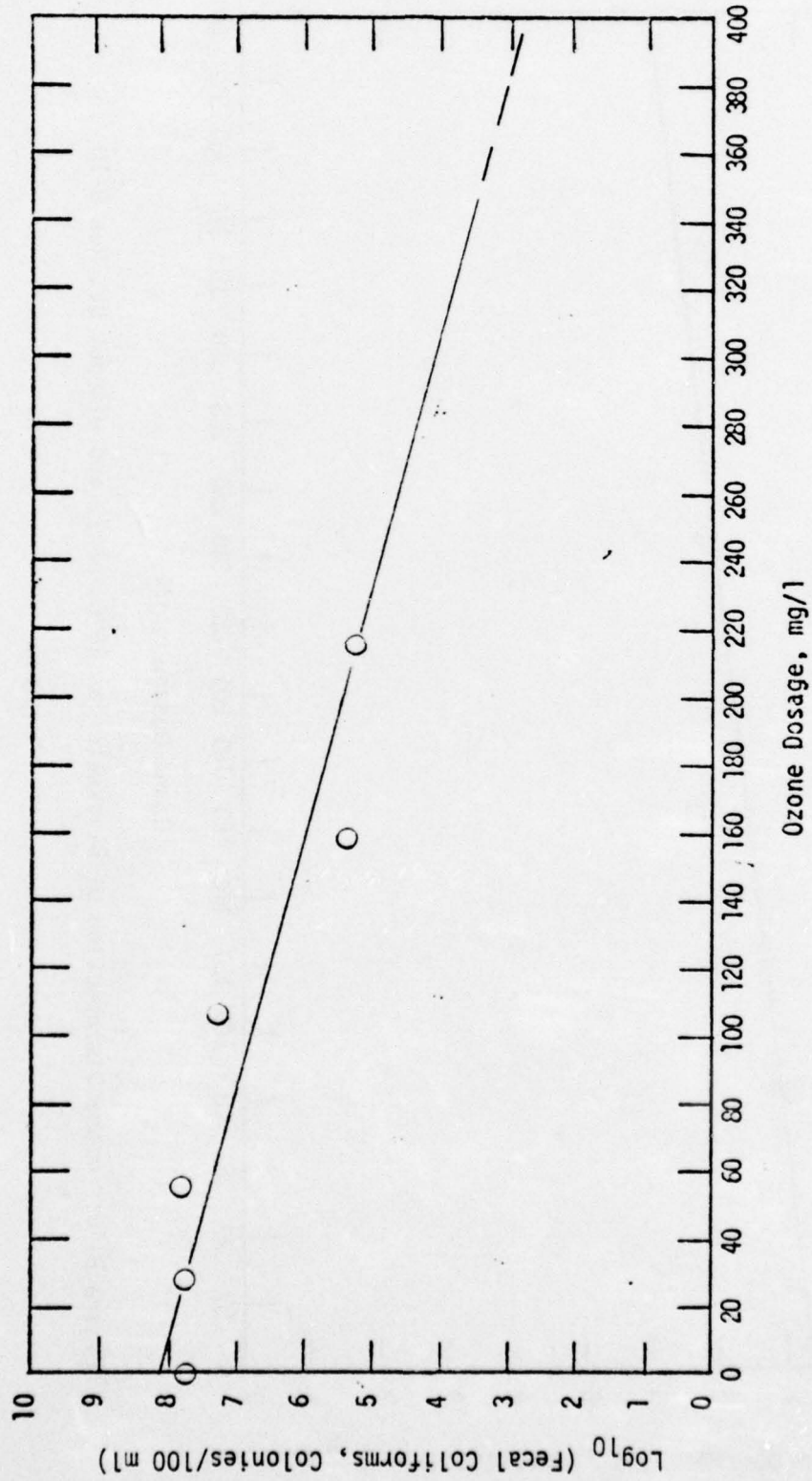


Figure B-11: Ozone Disinfection of Blackwater at 30°C, pH 7.6, and without UV; Run 0-11

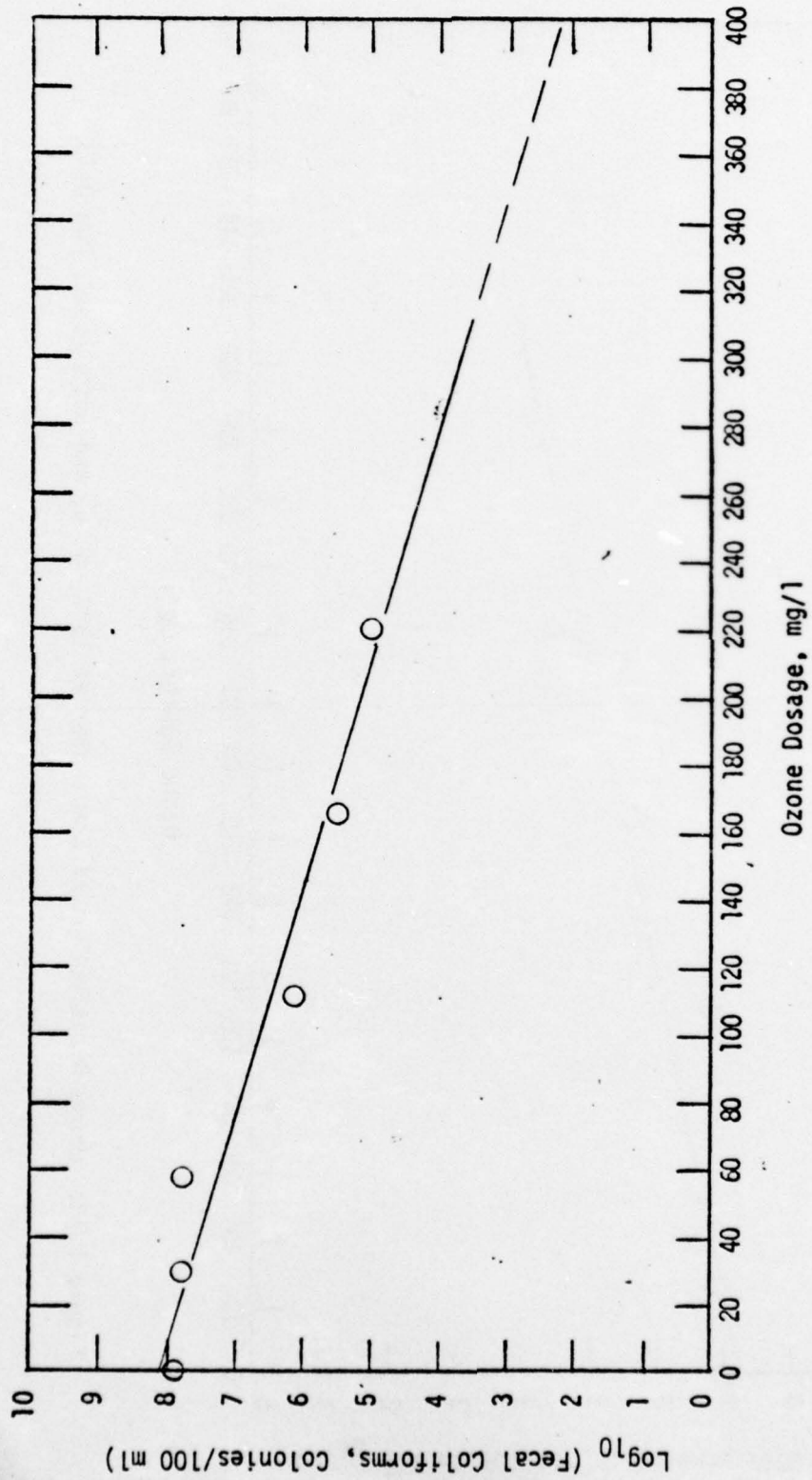


Figure B-12: Ozone Disinfection of Blackwater at 15°C, pH 8, and without UV; Run 0-12

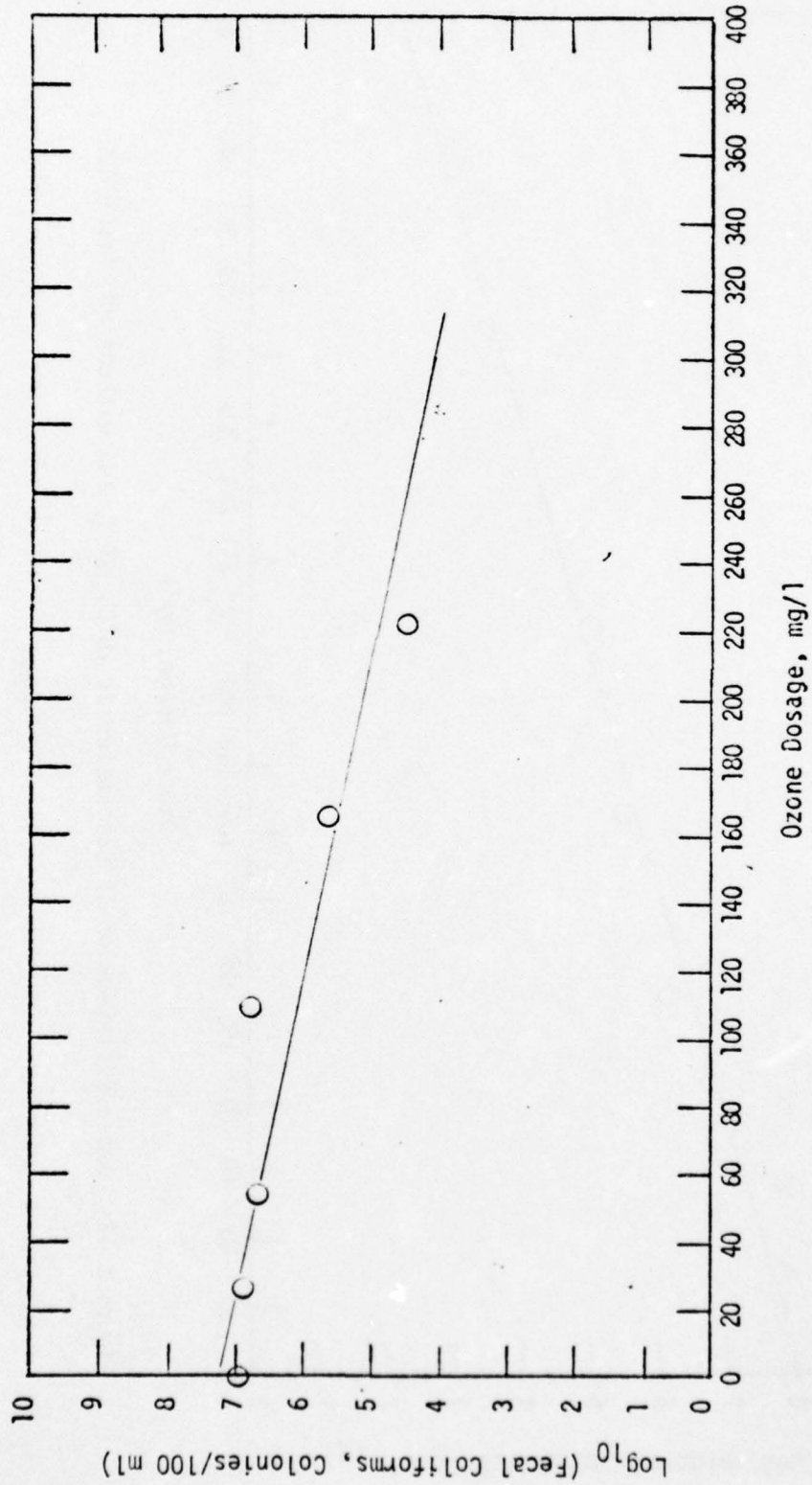


Figure B-13: Ozone Disinfection of Blackwater at 15°C, pH 6, and without UV; Run 0-13

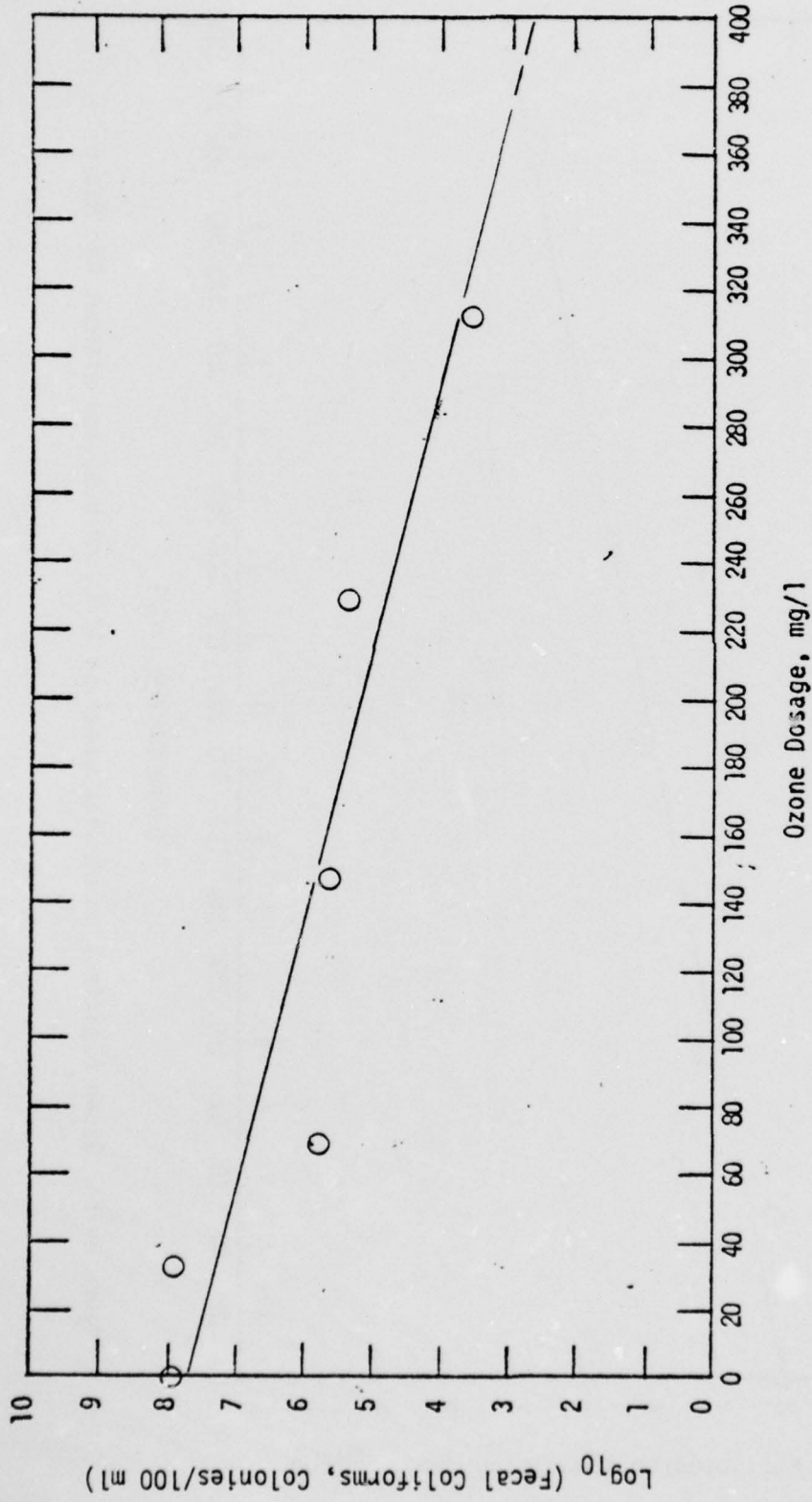


Figure B-14: Ozone Disinfection of Blackwater at 30°C, pH 6, and without UV; Run 0-14

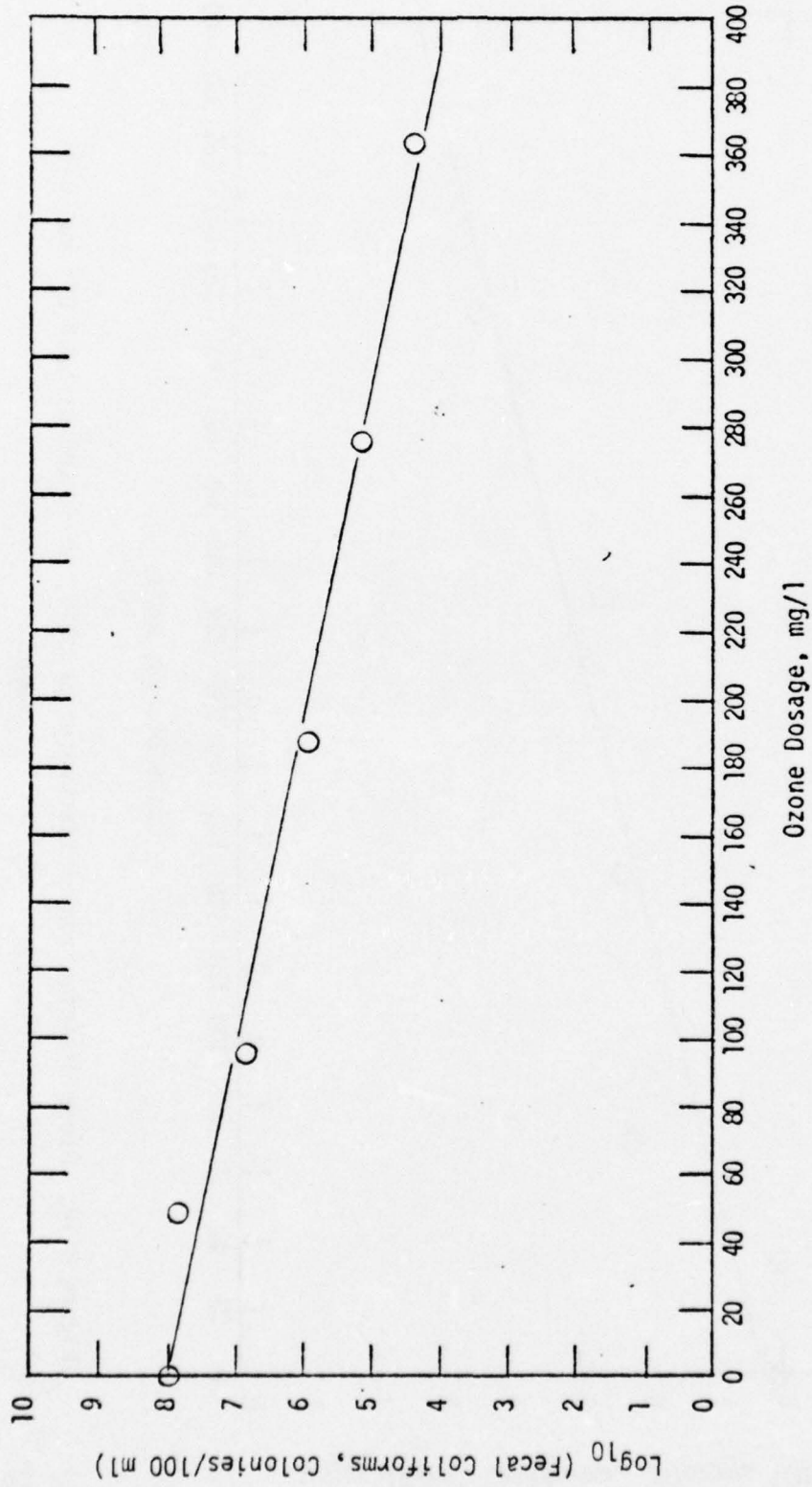


Figure B-15: Ozone Disinfection of Blackwater at 15°C, pH 8.5, and without UV; Run 0-15

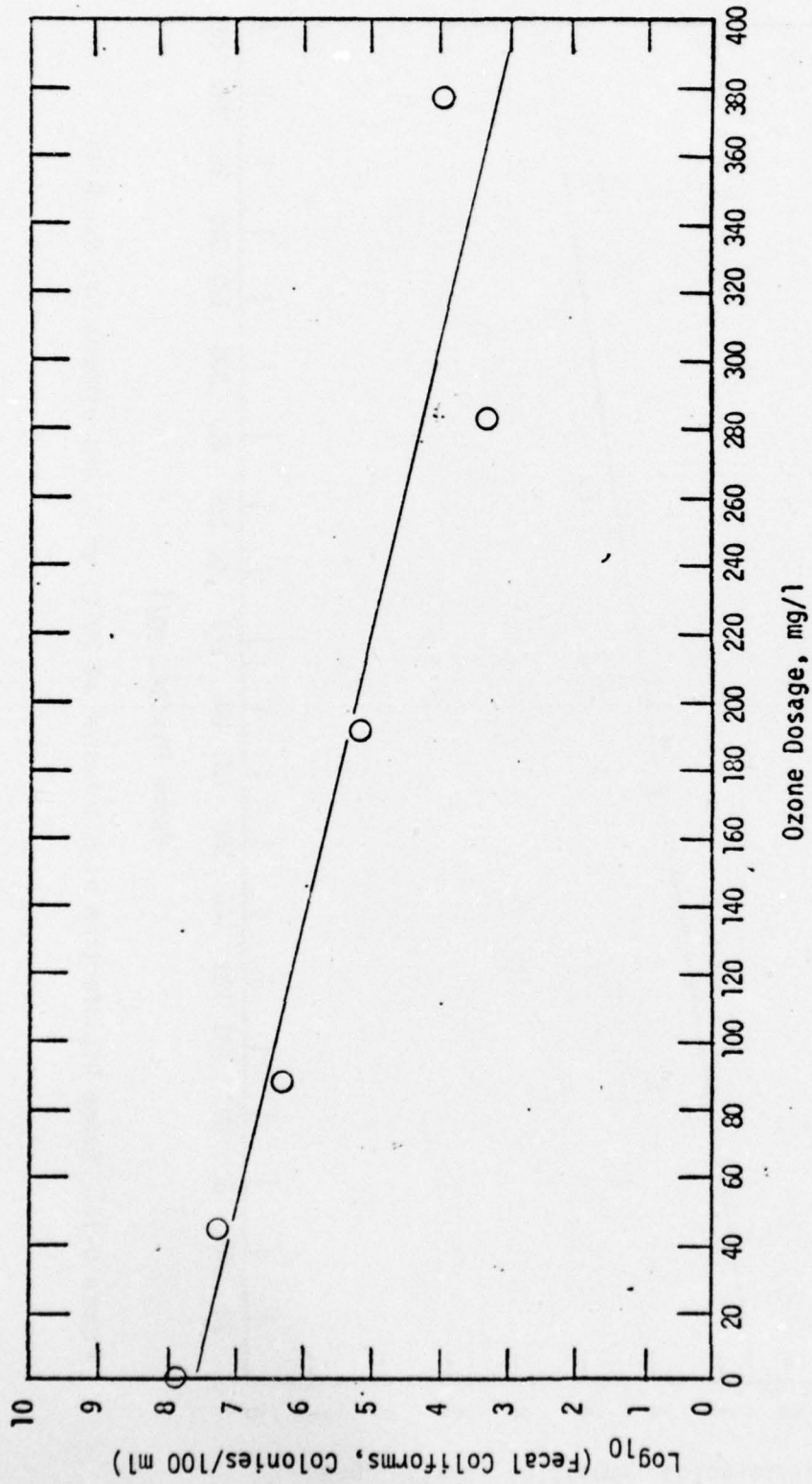


Figure B-16: Ozone Disinfection of Blackwater at 30°C, pH 8.2, and without UV; Run 0-16

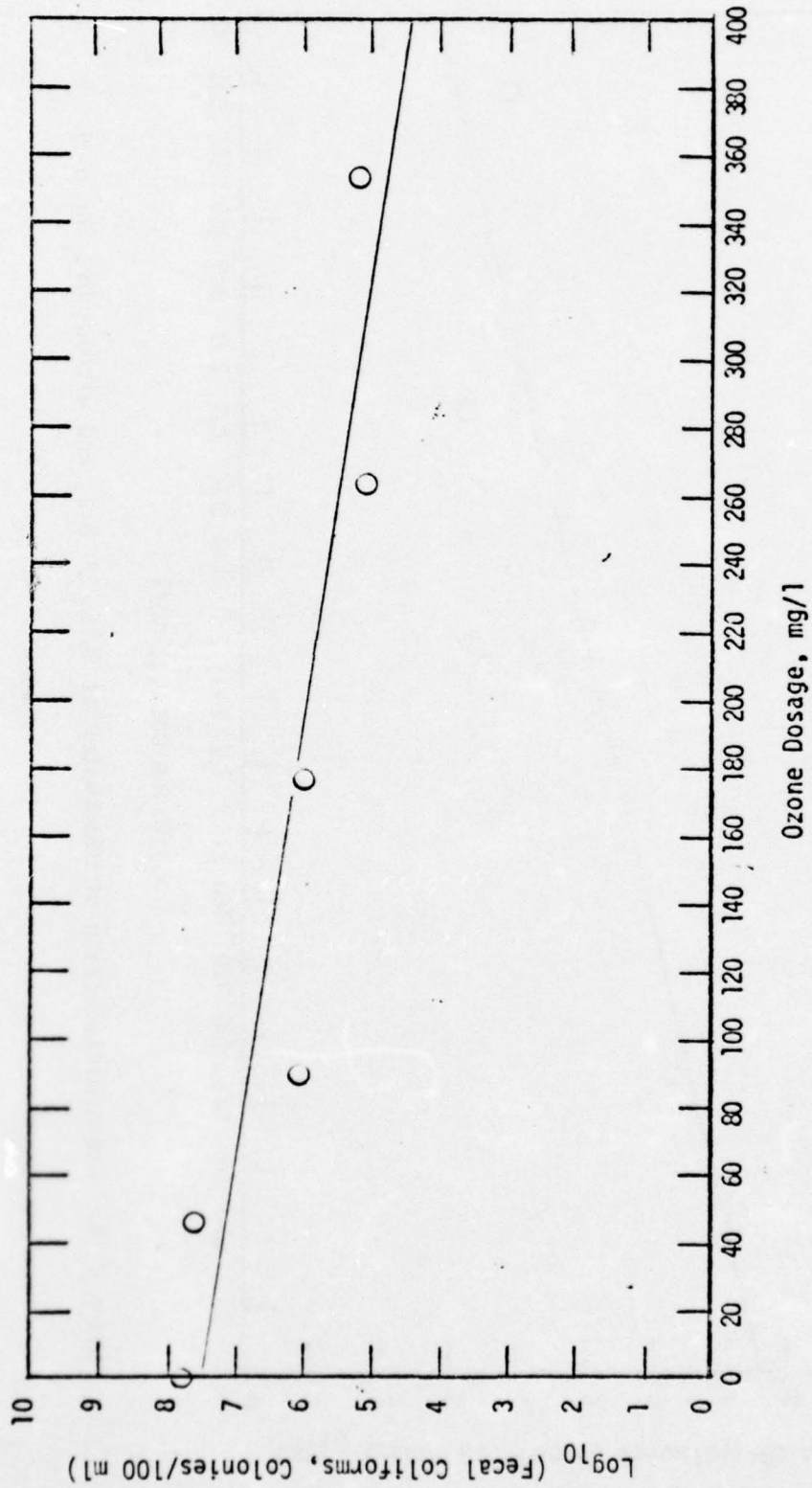


Figure B-17: Ozone Disinfection of Blackwater at 30°C, pH 9, and without UV; Run 0-17

APPENDIX C
DATA FOR CHLORINE DISINFECTION OF BLACKWATER

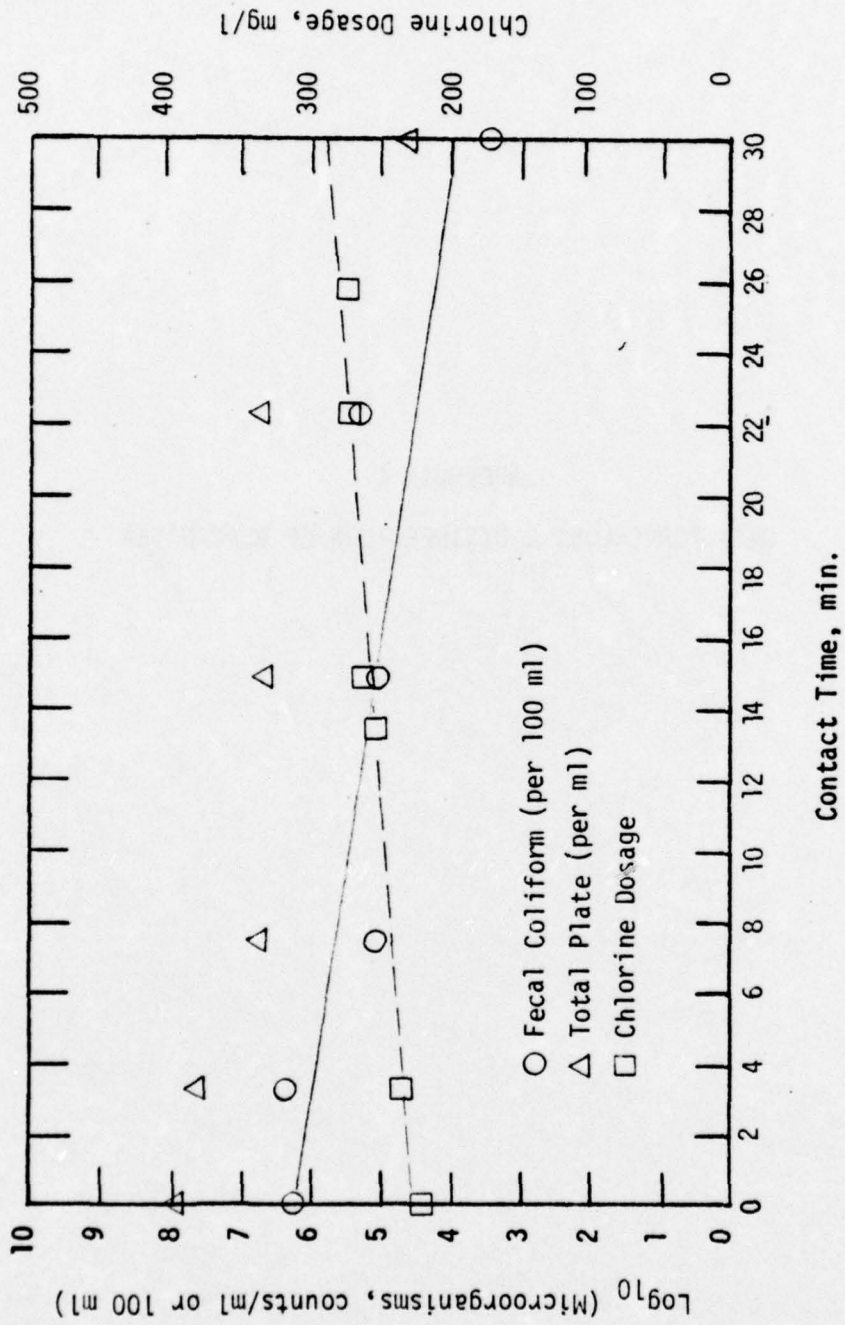


Figure C-1: Chlorine Disinfection of Blackwater at 30°C, and pH 9; Run C-1

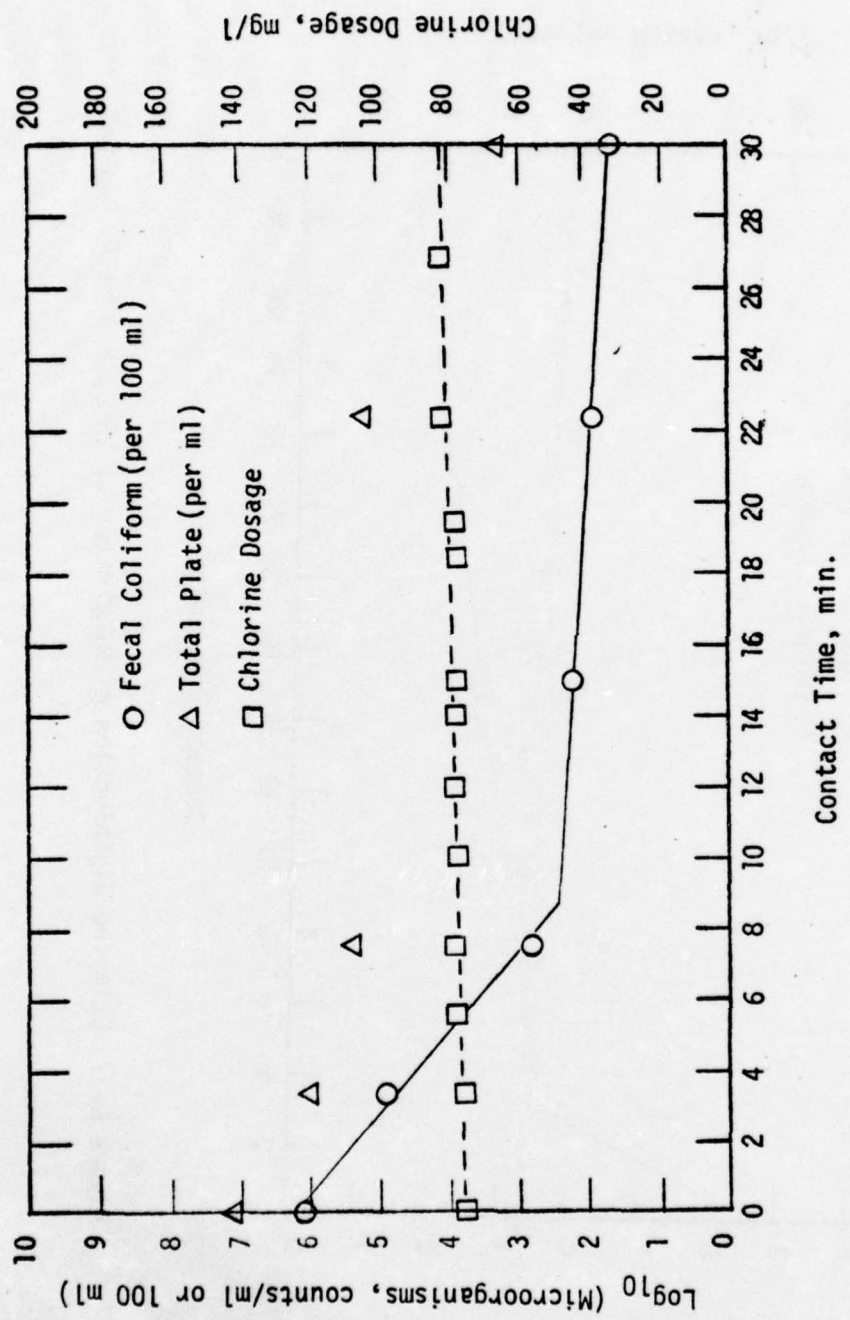


Figure C-2: Chlorine Disinfection of Blackwater at 15°C, and pH 5; Run C-2

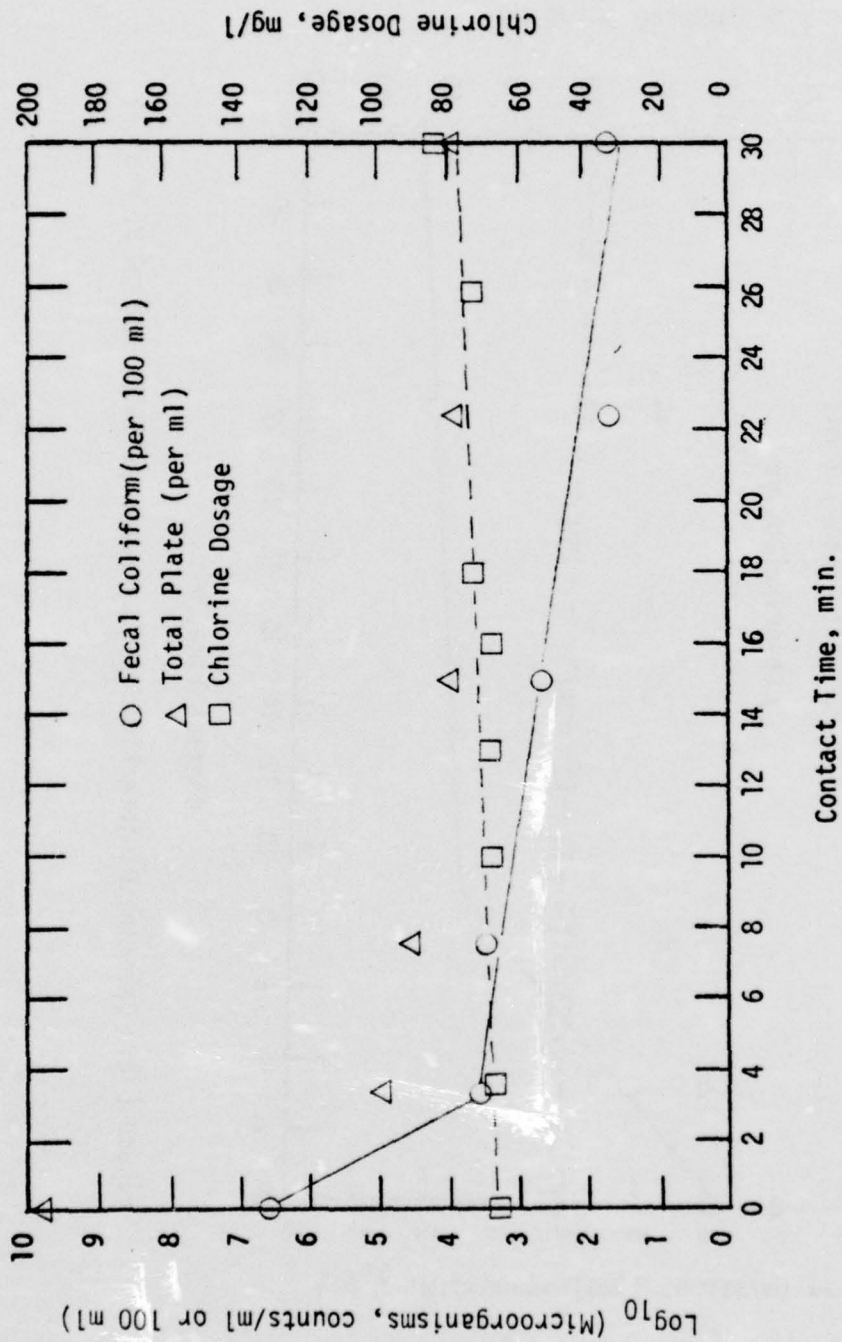


Figure C-3: Chlorine Disinfection of Blackwater at 15°C, and pH 7; Run C-3

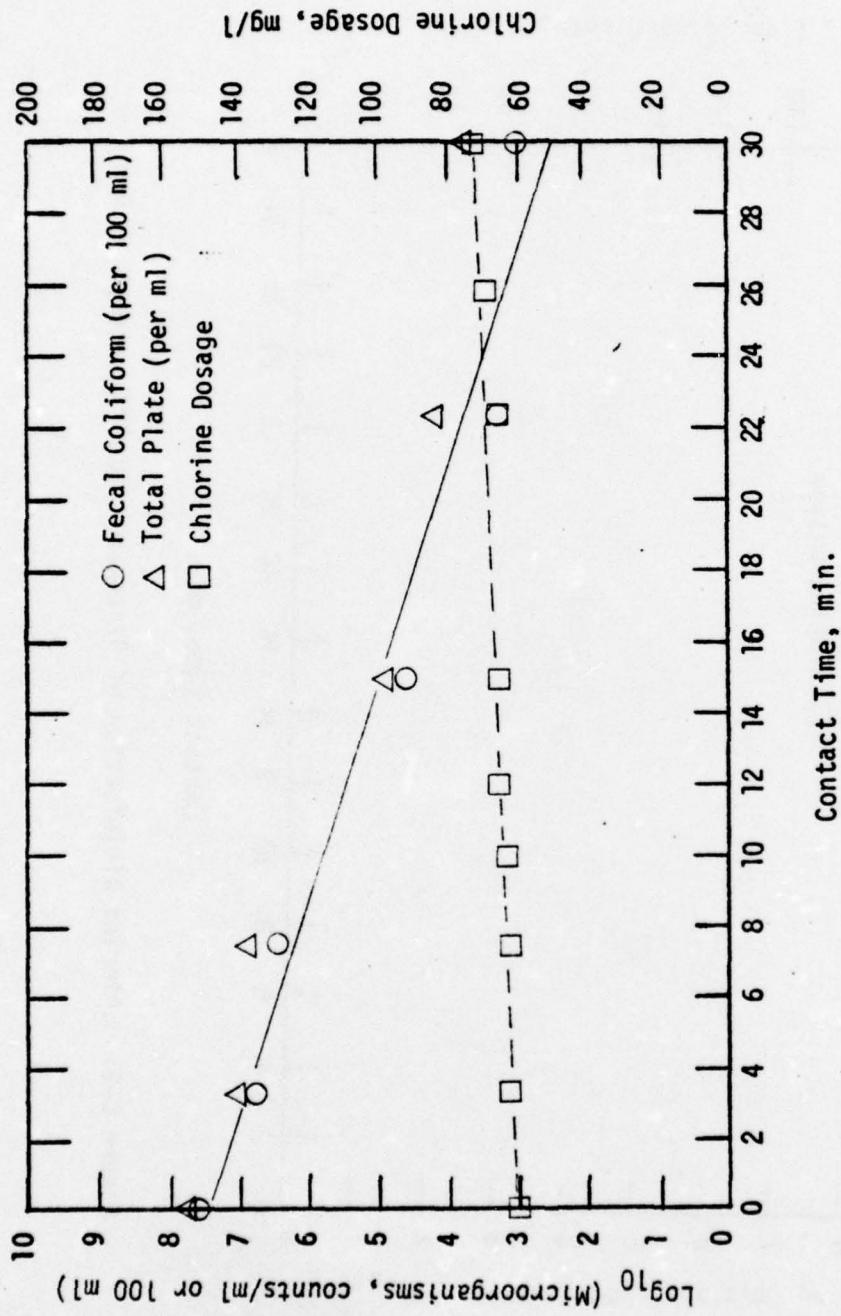


Figure C-4: Chlorine Disinfection of Blackwater at 30°C, and pH 5; Run C-4

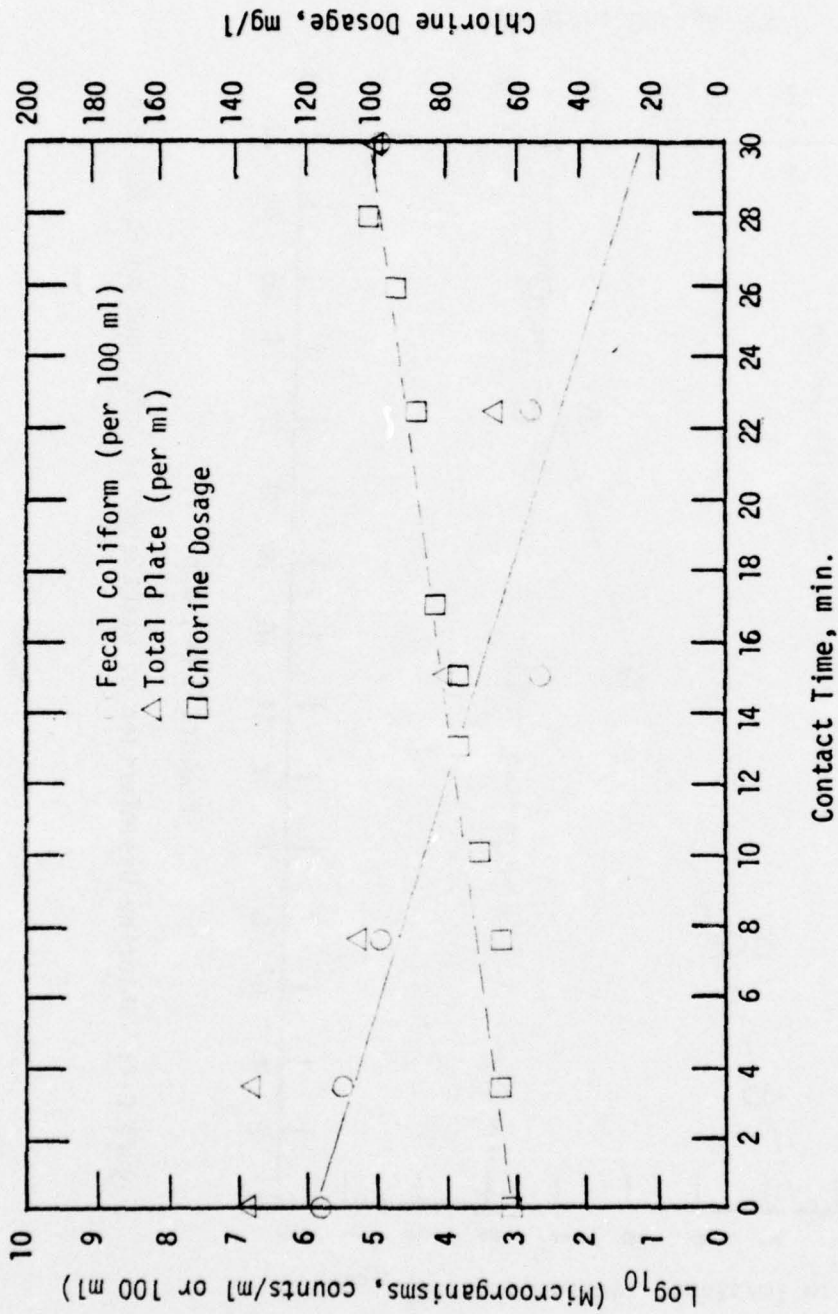


Figure C-5: Chlorine Disinfection of Blackwater at 30°C, and pH 7; Run C-5

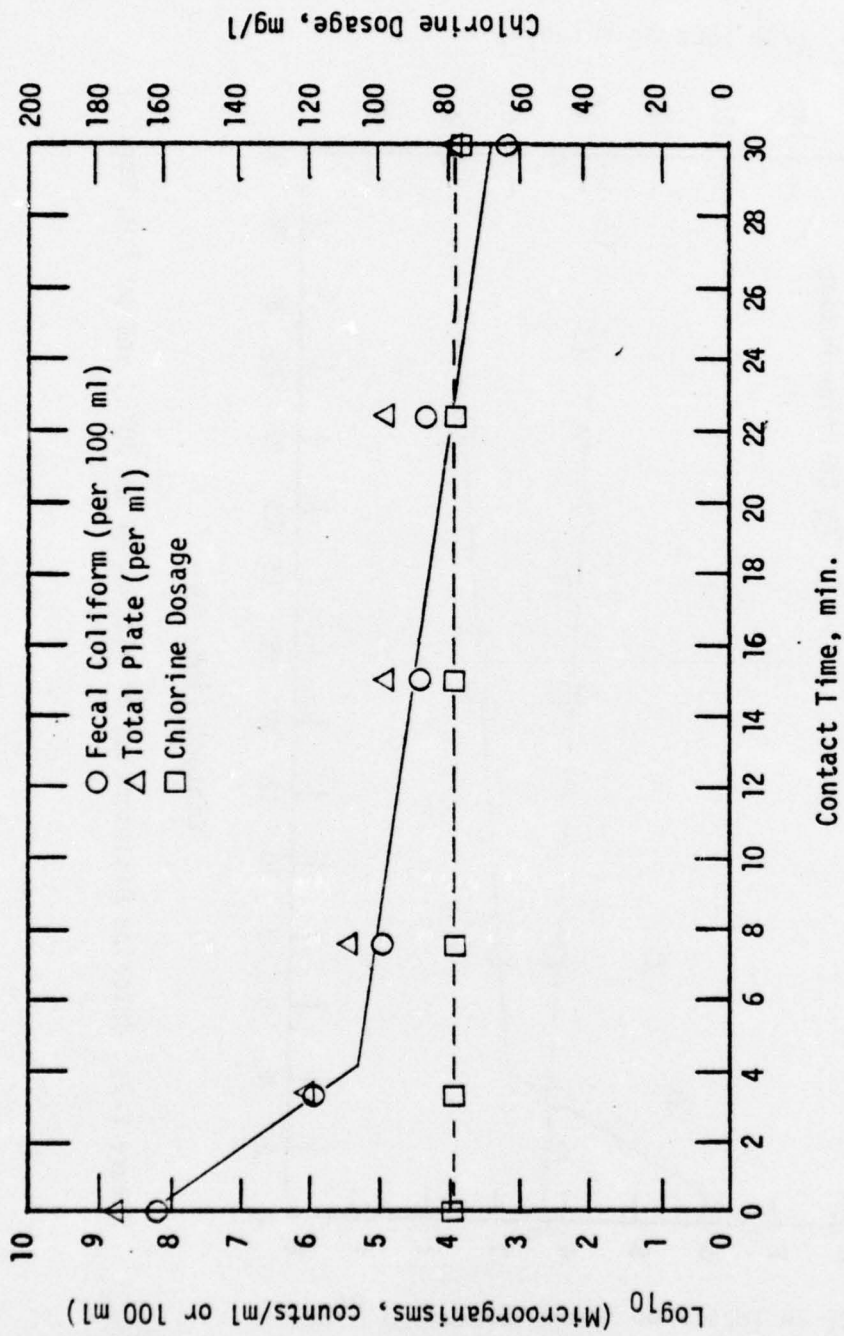


Figure C-6: Chlorine Disinfection of Blackwater at 15°C, and pH 9; Run C-6

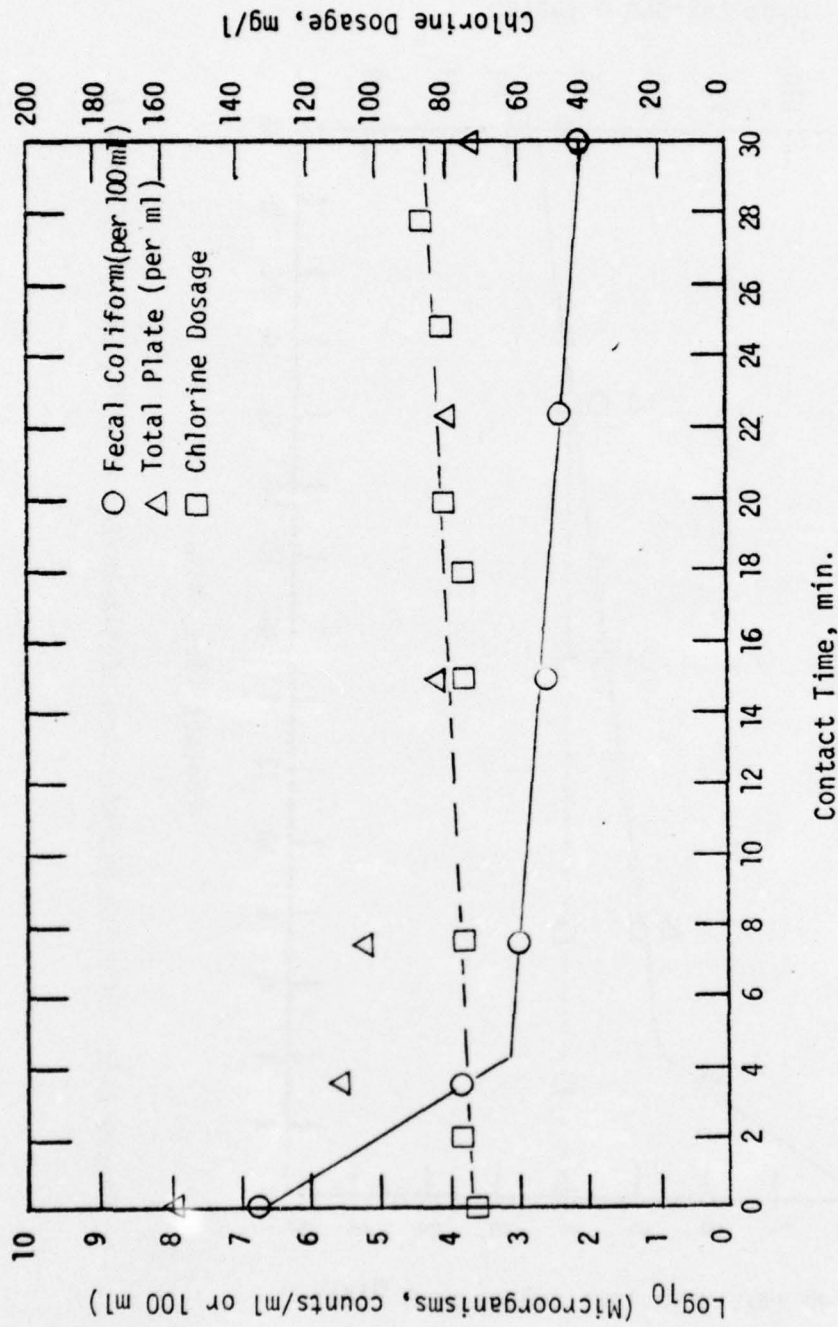


Figure C-7: Chlorine Disinfection of Blackwater at 30°C, and pH 7.0; Run C-7

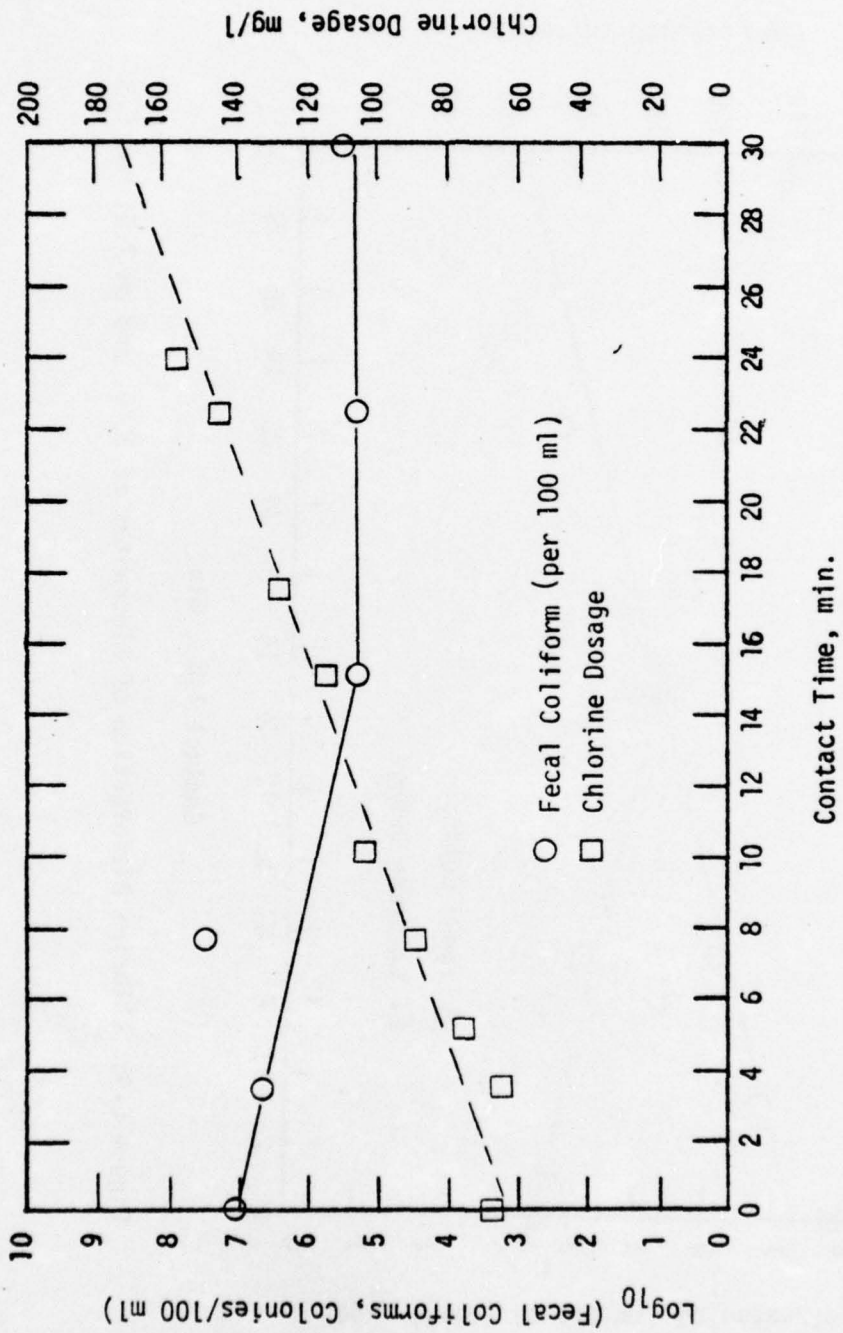


Figure C-8: Chlorine Disinfection of Blackwater at 30°C, and pH 5; Run C-8

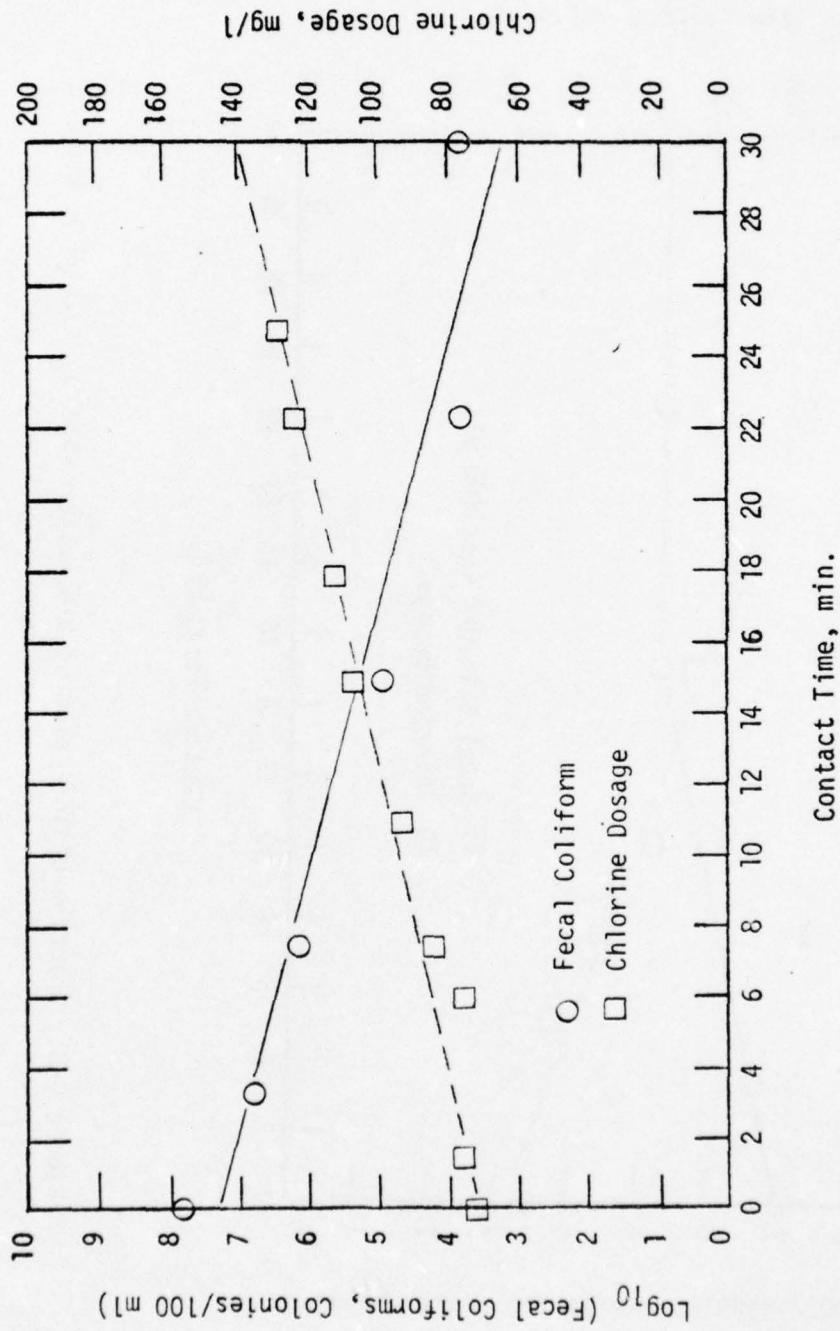


Figure C-9: Chlorine Disinfection of Blackwater at 30°C, and pH 7.6; Run C-9

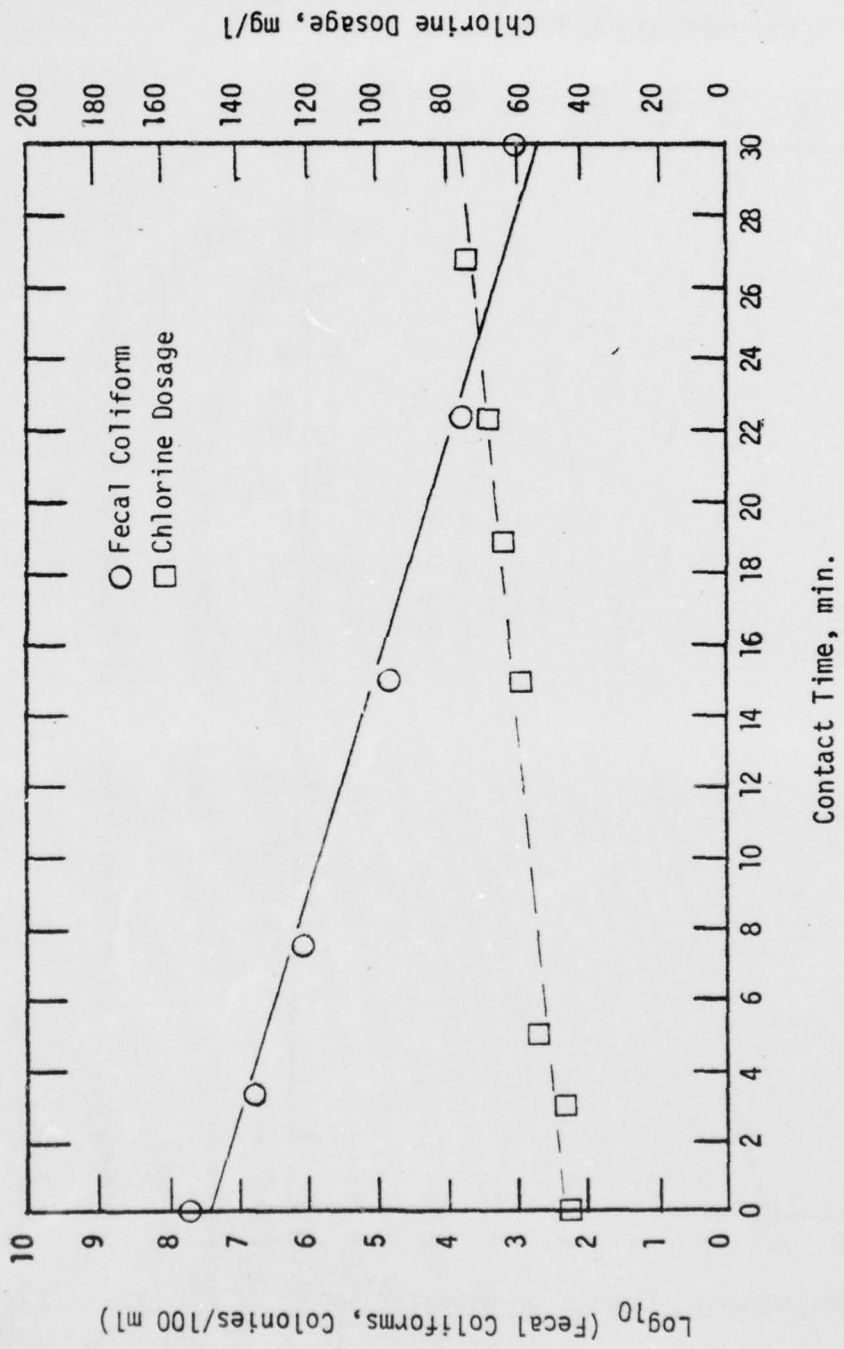


Figure C-10: Chlorine Disinfection of Blackwater at 15°C, and pH 8.0; Run C-10

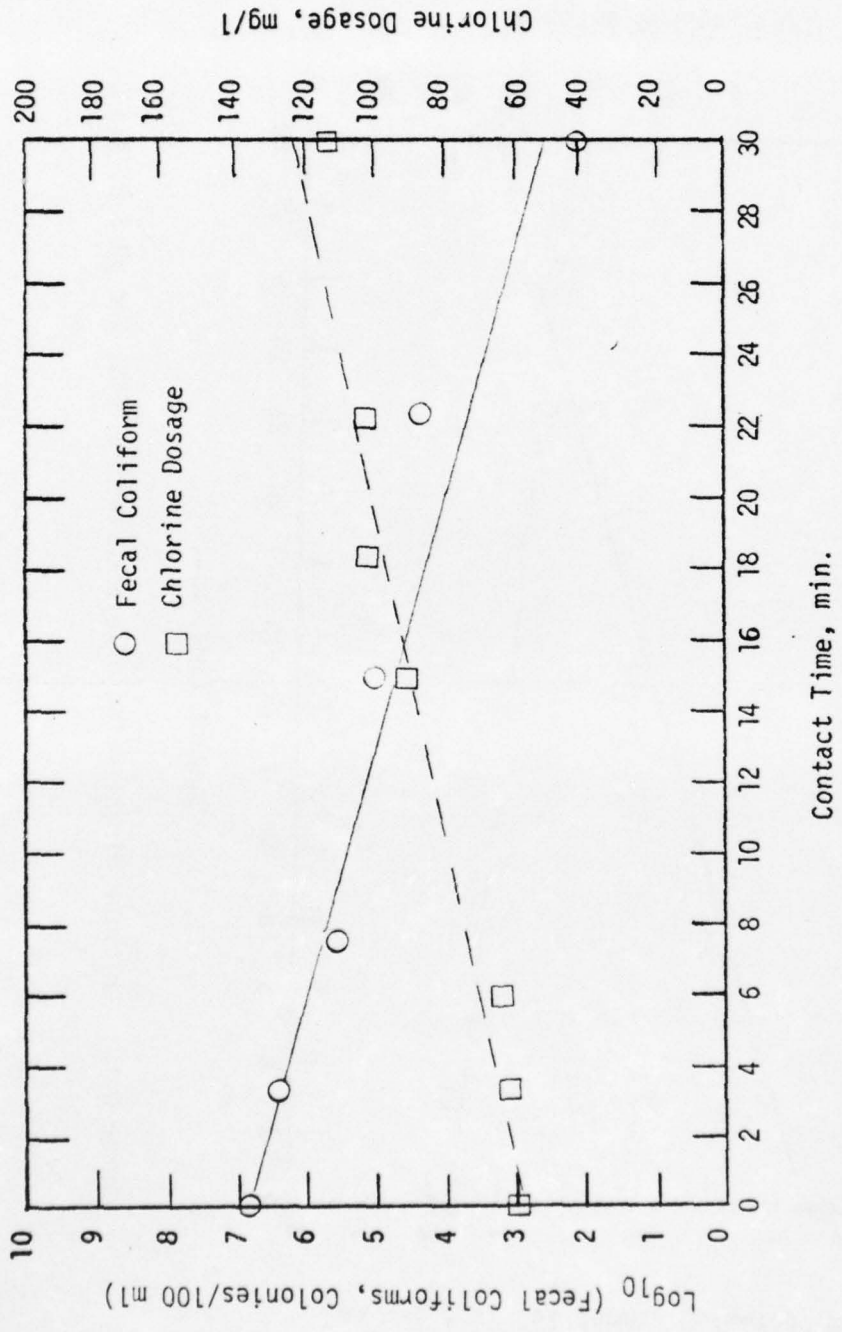


Figure C-11: Chlorine Disinfection of Blackwater at 15°C, and pH 6; Run C-11

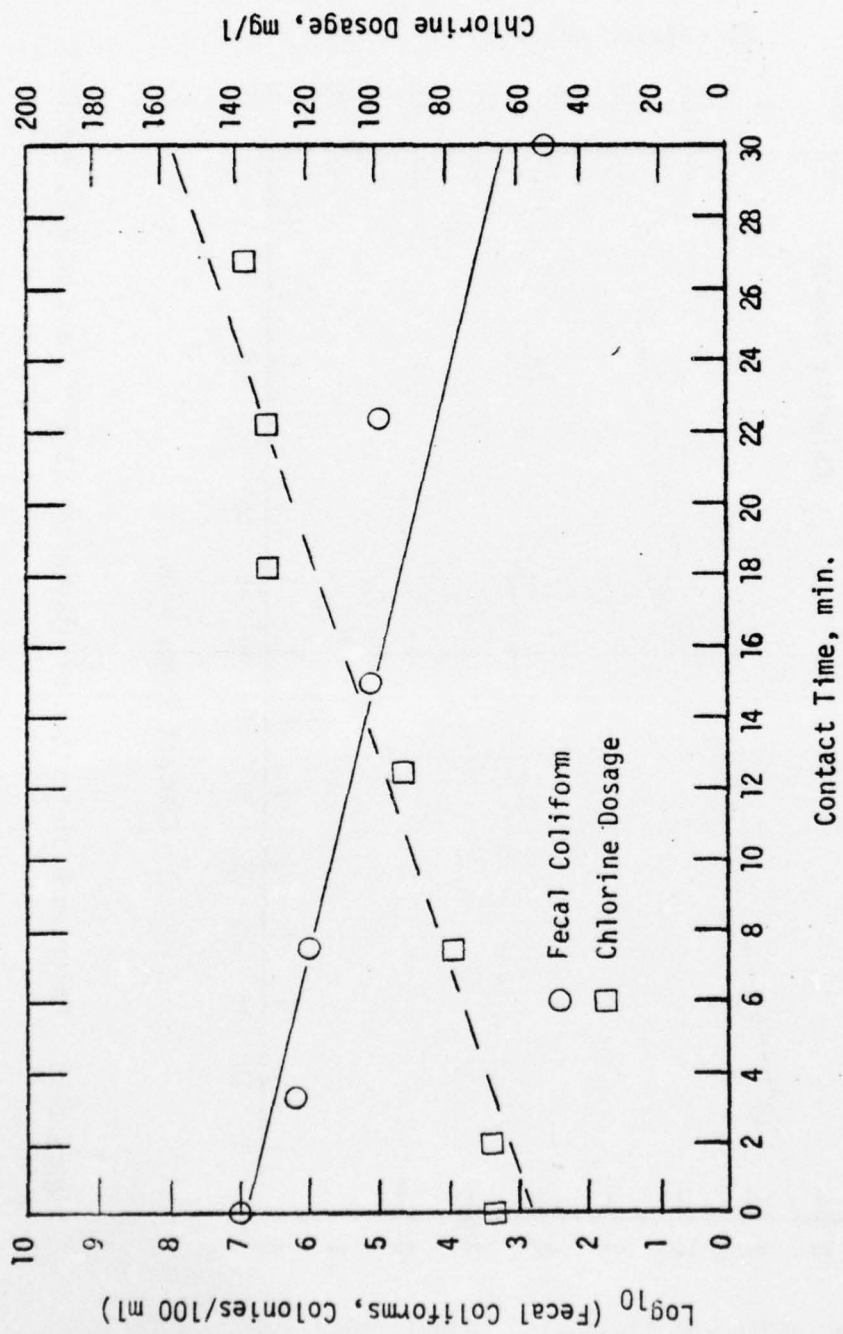


Figure C-12: Chlorine Disinfection of Blackwater at 30°C, and pH 6; Run C-12

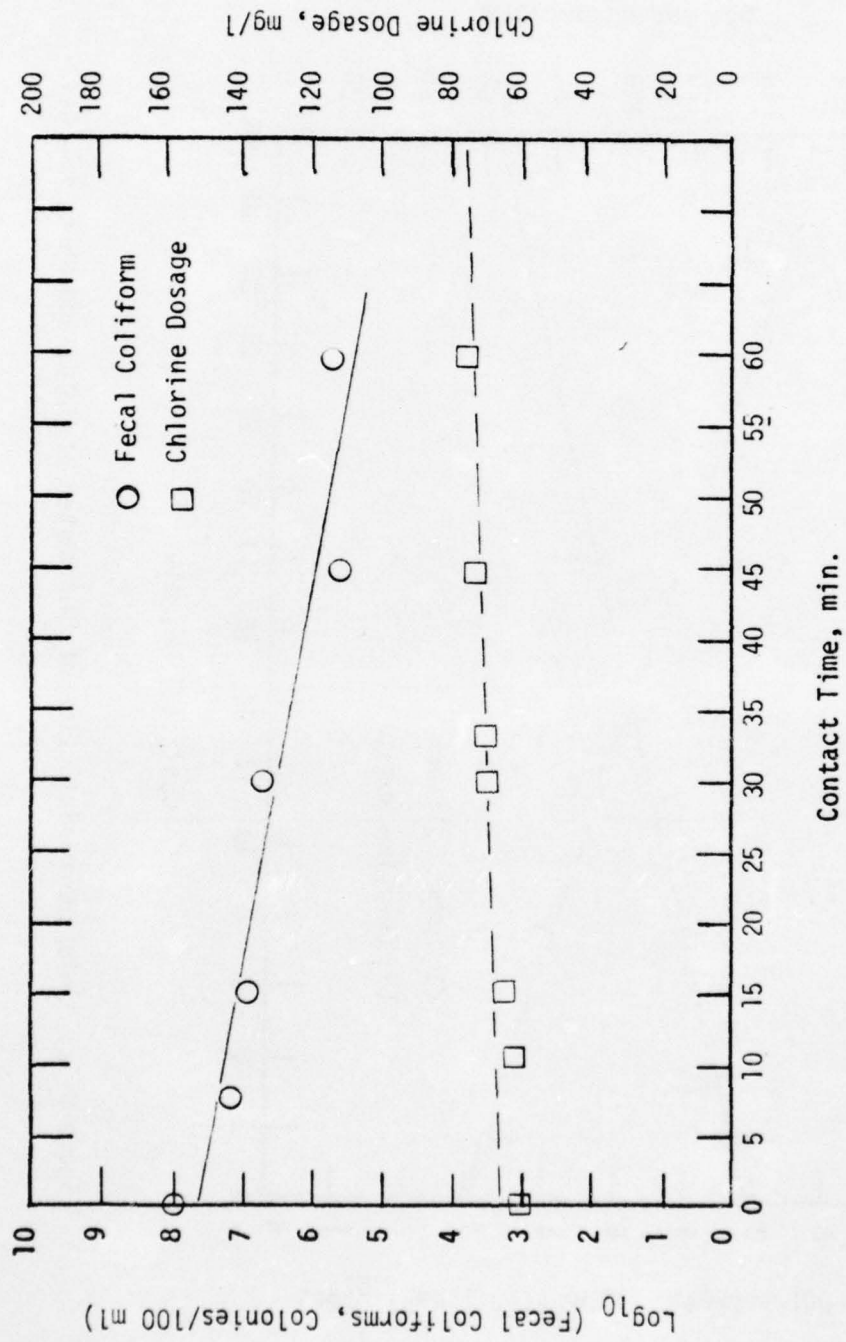


Figure C-13: Chlorine Disinfection of Blackwater at 15°C, and pH 8.4; Run C-13

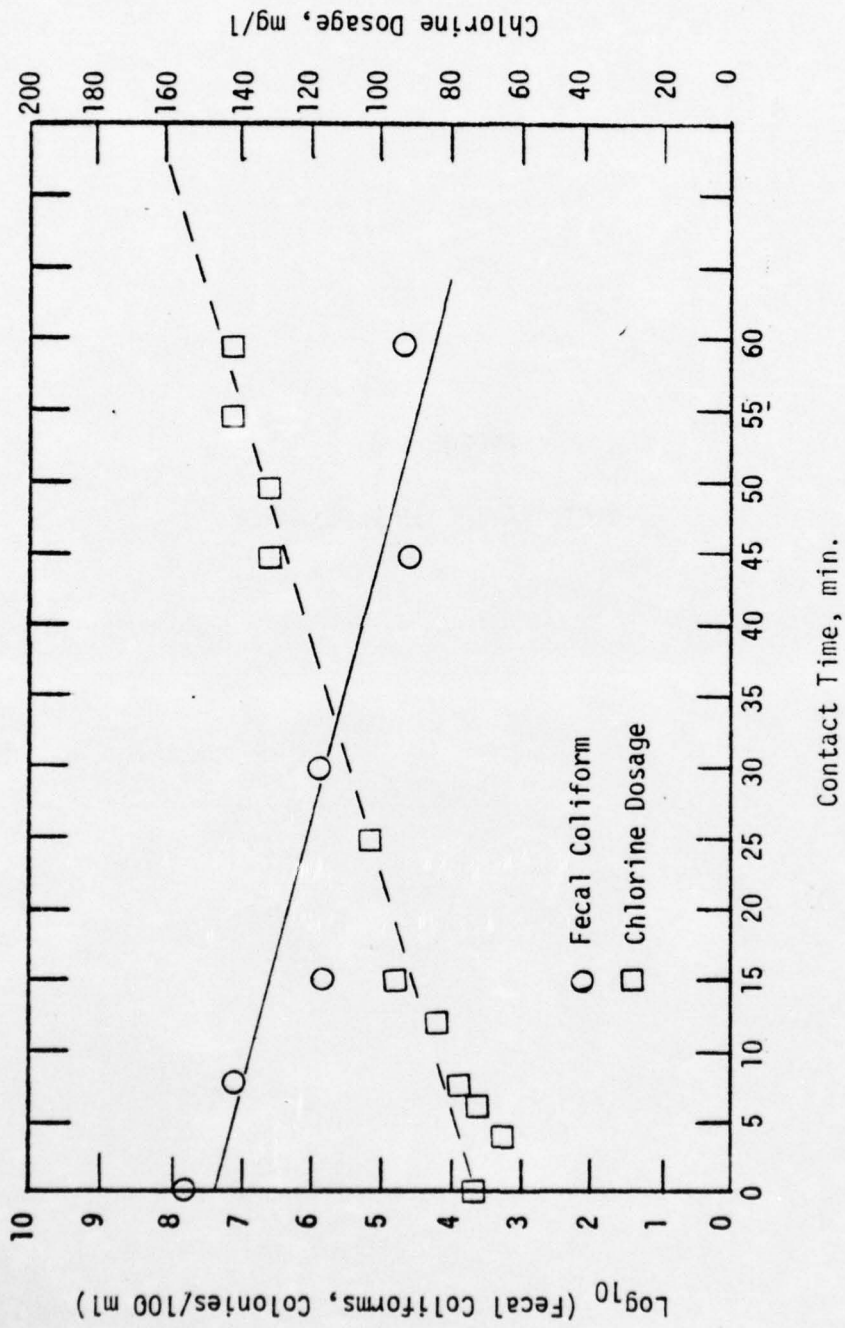


Figure C-14: Chlorine Disinfection of Blackwater at 30°C, and pH 8.1; Run C-14

APPENDIX D
ULTRAFILTRATION OF BLACKWATER

Test Summary

Ultrafiltration of Blackwater

I. INTRODUCTION

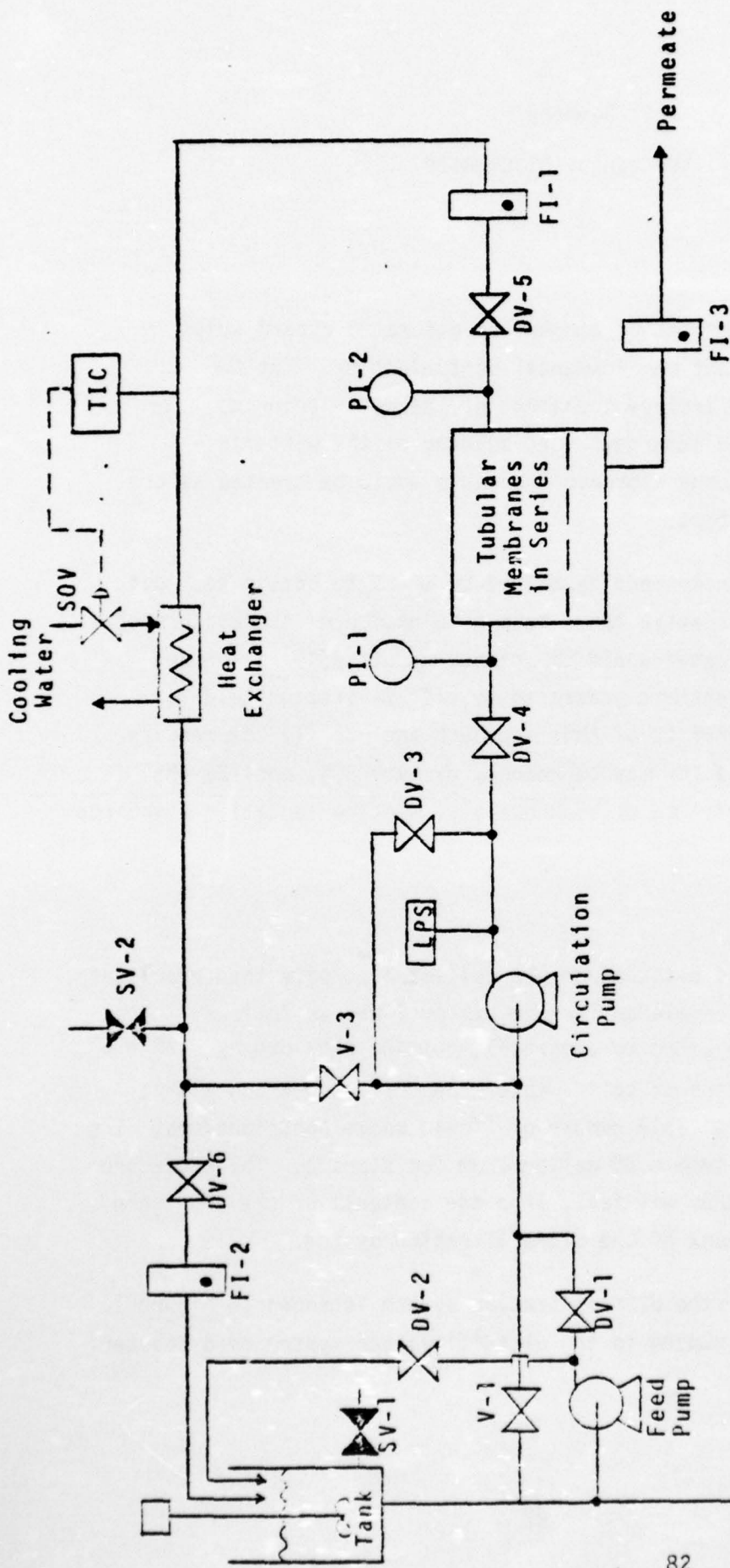
A method for the treatment of blackwater generated aboard ships must be developed to prevent environmental contamination. The two approaches to the problem include treatment of the waste prior to discharge overboard, or "no discharge," i.e. holding of the waste in holding tanks. In the second approach the waste would be treated ashore when the ship returns to port.

The purpose of the experiment described here was to obtain test data for evaluation of an alternative based on a combination of these approaches. In this alternative blackwater would be treated by ultrafiltration and discharged, with the concentrate generated by ultrafiltration held for discharge ashore. The benefits of this approach include (1) the requirement for holding tank capacity may be reduced by over 90%, and (2) the water discharged at sea will be of high quality, meeting tentative standards for discharge.

II. EXPERIMENTAL

A 55 gallon sample of black water was collected on site then processed by ultrafiltration. The sample collection protocol was as follows. Nine gallons of tap water were added to a portable commode provided by USAMERDC. Three separate contributions of solid waste were collected along with a proportionate but uncontrollable number of liquid waste contributions. The commode was then emptied into a 55 gallon drum for storage. The procedure was continued until the drum was full, then the contents of the drum were transferred to the feed tank of the ultrafiltration system.

A flow schematic for the ultrafiltration system is shown in Figure 1. The black water feed was pumped to the ultrafiltration system by a booster



Legend

- DV - Diaphragm Valve
- FI - Flow Indicator
- LPS - Low Pressure Switch
- PI - Pressure Indicator
- SOV - Solenoid Valve
- SV - Sample Valve
- TIC - Temperature Indicator Controller
- V - Ball Valves

FIGURE 1. ULTRAFILTRATION TEST SYSTEM FLOW SCHEMATIC
SYSTEM #1

pump. A centrifugal circulation pump was then used to pressurize the feed and pass it through the membrane modules. The circulation flow rate (30 gpm) and the inlet operating pressure (50 psig) were controlled by a pump bypass valve and a concentrate throttle valve. A low pressure switch prevented the pump from running dry. A temperature controller and heat exchanger were used to maintain the operating temperature at 75°F. The permeate flow rate was measured using a rotameter.

Two tests were performed. The first test was a batch concentration in which the concentrate was returned to the feed tank and the permeate collected in a separate tank. The second test was performed in a total recycle mode in which both the concentrate and the permeate were returned to the feed tank. In this test, the system was operated continuously with a feed that was approximately five times as concentrated as the initial feed. Membrane cleaning was not performed between the tests.

Two tubular noncellulosic UF membranes, both manufactured by Abcor, Inc., were tested:

- Abcor type HFD
- Abcor type HFM

The operating specifications for these two membranes are as follows:

	<u>HFD</u>	<u>HFM</u>
Maximum pressure	75 psig	60 psig
Allowable pH range	2-12	} pH 4-9 175°F pH 11 140°F pH 12.5 100°F
Maximum temperature	185°F	

In order to characterize the membrane rejection efficiency, samples of both feed and permeate were taken during the test and analyzed for turbidity, suspended solids, and fecal coliforms.

III. RESULTS AND DISCUSSIONS

UF membrane performance is characterized by solute rejection and membrane flux (capacity). Each will be discussed separately below.

A. MEMBRANE CAPACITY

The membrane fluxes obtained during the two experiments are shown in Figure 2. During the batch concentration test the flux for both membranes decreased as the concentration increased indicating that the capacity of the membranes is dependent on concentration. During the total recycle test the flux level for both membranes was high and steady. The steady flux is very significant since it indicates that a low frequency of membrane cleaning is required.

The effect of concentration on flux is shown in Figure 3. The data indicate that membrane flux decreases linearly with the log of concentration. This is typical of ultrafiltration processes. If the curve is extrapolated to a concentration factor of 20 and an average flux calculated over that concentration range (1-20 X feed concentration), the following fluxes are determined:

HFD membrane	35 gal/ft ² -day
HFM membrane	37 gal/ft ² -day

These flux levels can be used to design a system in which the waste volume which must be stored is reduced to 5% of the waste produced.

B. MEMBRANE REJECTION EFFICIENCY

The analyses taken during the two tests are shown in Table 1. Rejection efficiencies (defined as $R = 100(1 - C_p/C_f)$ where C_p = concentration in the permeate and C_f = concentration in the feed) were excellent. Rejection of turbidity, suspended solids, and fecal coliforms was greater than 99% in all cases. The ranges of permeate analyses were as follows:

FIGURE 2. TUBULAR ULTRAFILTRATION OF BLACK WATER: FLUX VERSUS TIME

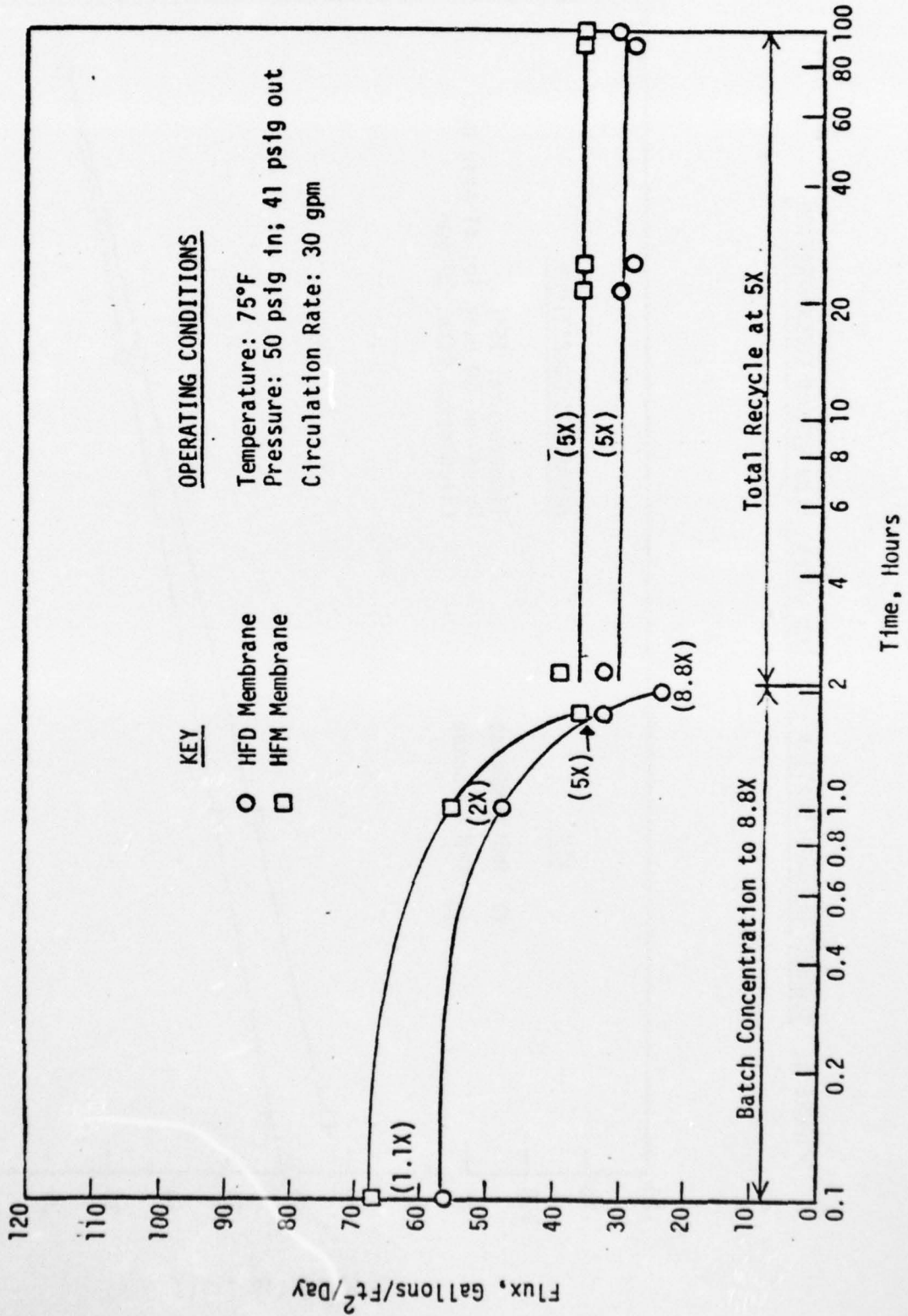


FIGURE 3. TUBULAR ULTRAFILTRATION OF BLACK WATER: FLUX VERSUS CONCENTRATION

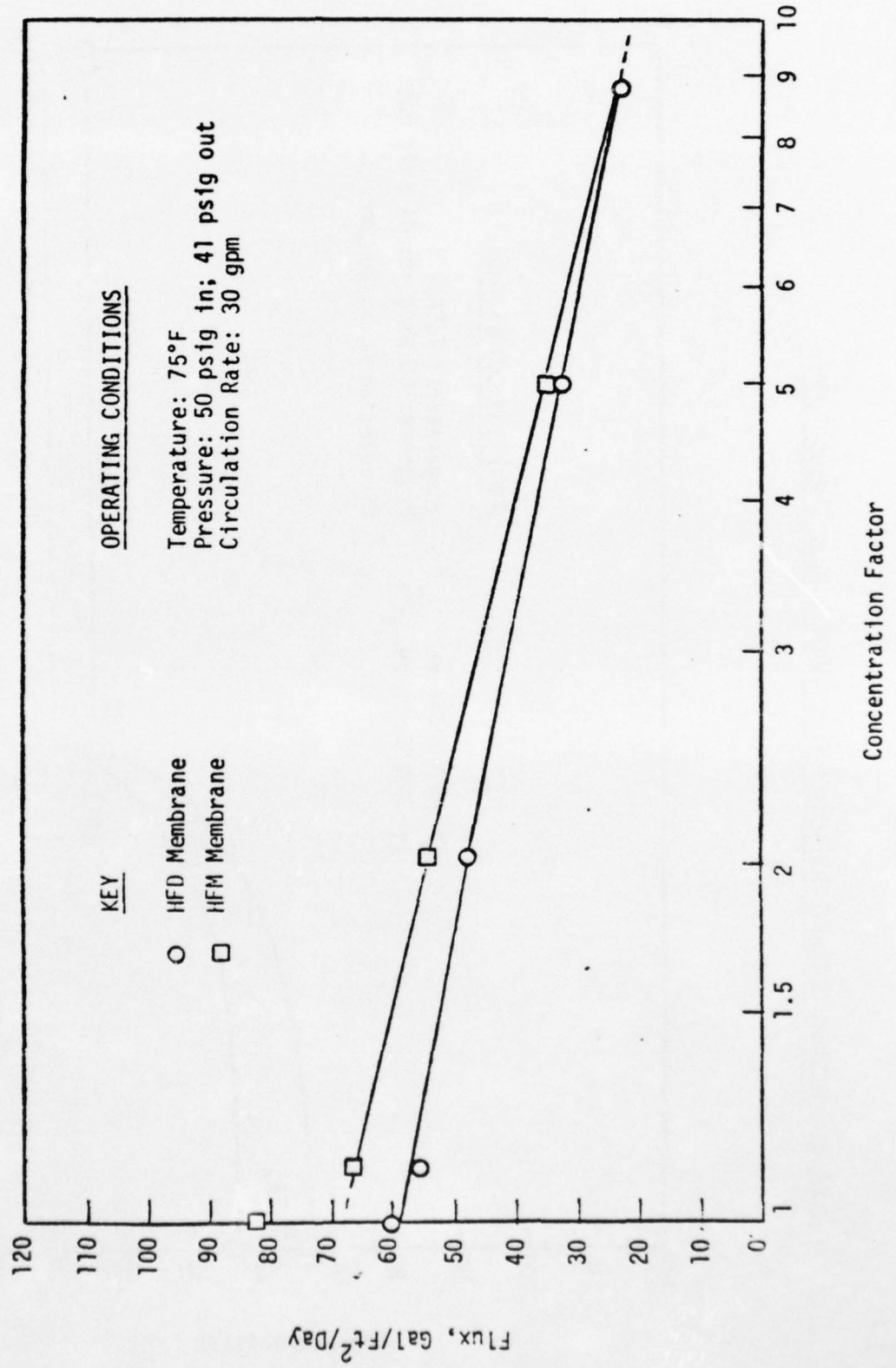


TABLE 1

ANALYSES

Batch Concentration Test

Turbidity (NTU) _____ Suspended Solids (mg/lit) _____ Fecal Coliforms (colonies/100 ml) _____

Concentration Factor	Turbidity (NTU)		Suspended Solids (mg/lit)		Fecal Coliforms (colonies/100 ml)				
	Feed	HFD Perm	HFM Perm	Feed	HFD Perm	HFM Perm			
1	700	4.0	1.2	2060	16	14	75 X 10 ⁶	1500	1800
2	1700	0.82	0.56	4200(1)	16	13	---	1600	1700
5	3500	1.6	1.5	8150(1)	15	16	---	1700	1600
8.8	4500	0.55	0.45	11850(1)	26	19	---	650	150

Total Recycle Test

Turbidity (NTU)

Time	Feed	HFD Perm	HFM Perm
21.2		0.77	0.56
25.0		0.60	0.50
90.6		0.68	0.71
98.2		0.57	0.48

(1) Samples very difficult to filter. May be in error.

Turbidity (NTU)	0.5 - 4.0
Suspended solids (mg/lit)	13 - 26
Fecal coliforms (colonies/100 ml)	150 - 1800

IV CONCLUSIONS

These results indicate that ultrafiltration is a viable technology for the treatment of black water generated aboard ship. High, stable fluxes and excellent rejection efficiencies are attainable when concentrating the waste to 8.8 times its original concentration. Further concentration appears to be feasible.

AD-A033 734

ABCOR INC WILMINGTON MASS WALDEN RESEARCH DIV
EVALUATION OF OZONATION AND CHLORINATION FOR DISINFECTION OF BL--ETC(U)
DEC 76 K J MCNULTY, R L GOLDSMITH

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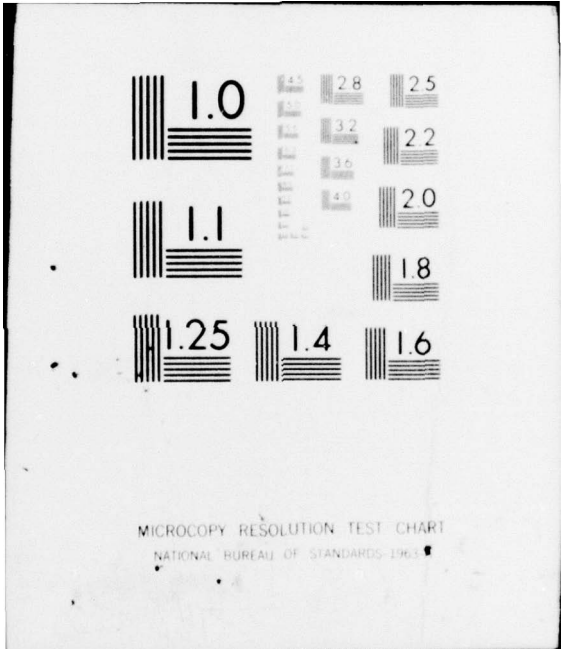
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