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A PILOT PLANT TRIAL FOR OZONE STERILIZATION OF FISH HATCHERY WATER

by

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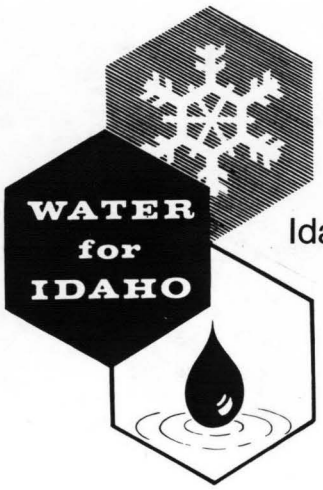

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TABLE OF CONTENTS

	Page
Approval Page	ii
Acknowledgements	iv
List of Figures	v
List of Tables	viii
Abstract	1
I. Introduction	4
II. Analytical Procedures	10
III. Equipment Description	15
IV. Laboratory Studies	21
V. Pilot Plant Studies	31
VI. Results	34
VII. Conclusion	38
VIII. Recommendations	41
Bibliography	42
Figures	44
Appendices	
A. Data Tables	77
B. Chronological Account Ozone Pilot Plant Continuous Operation	100
C. Sample Calculation-Ozone Concentration in Gas Leaving Ozone Generator	107
D. Sample Calculation-Mass Balance on Integrated Pilot Plant	109
E. Ozone System-Preliminary Design Cost Analysis	110
F. Ultraviolet System-Preliminary Design Cost Analysis	112

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LIST OF FIGURES

Figure Number	Title	Page
1	Algae Growth on Ultraviolet Light Sterilizer at Dworshak National Fish Hatchery During Peak Algae Growth Period - Spring	44
2	Water Flow Schematic - Dworshak National Fish Hatchery	45
3	Laboratory Apparatus for Calibration of Ozone Generator	46
4	Calibration Curve - Ozone Generator Oxygen Feed	47
5	Laboratory Tests for Bacteria Survival in Ozonated Environment Bacillus Polymyxas Spores	48
6	Laboratory Tests for Bacteria Survival in Ozonated Environment Aeromonas Liquifaciens	49
7	Ozone Decay in Raw Dworshak River Water	50
8	Ozone Affects on Algae	51
9	Oxygen Affects on Algae	52
10	Contact Column	53
11	Flow Schematic Ozone Pilot Plant at Dworshak N.F.H.	54
12	Flow Schematic - Existing Biofilter Pilot Plant	55
13	Flow Schematic - Integrated Pilot Plant Makeup Water Ozone Treatment	56
14	Flow Schematic - Integrated Pilot Plant Recycle Water Ozone Treatment	57
15	Residual Ozone in Liquid Measured at Ozone Pilot Plant Column Outlet	58

LIST OF FIGURES, Continued

Figure Number	Title	Page
16	Microscope View - Steelhead Fry Control Fish - First Gill Arch Prior to Placement in Pilot Plant	59
17	Microscope View - Steelhead Fry Post Ozone Run - Pre-Mortality Study First Gill Arch	60
18	UV System Outlet Total Bacteria Count During Continuous Ozonation Run	61
19	Total Bacteria Count-Ozone Column Outlet During Continuous Ozonated Run	62
20	Total Bacteria During Continous Ozonation Run. Plate Counts - Average of Three Plates Per Sample	63
21	Biofilter Pilot Plant Nitrate Concentrations Before and During Continuous Ozonation Trial Run	64
22	Biofilter Pilot Plant Ammonia Concentrations Before and During Ozonation Trial Run	65
23	Biofilter Pilot Plant Nitrate Concentrations Before and During Ozonation Trial Run	66
24	Biofilter Pilot Plant Total Organic Nitrogen Concentration Before and During Ozonation Trial Run	67
25	Biofilter Pilot Plant Biochemical Oxygen Demand Before and During Ozonation Trial Run	68
26	Biofilter Pilot Plant Alkalinity Before and During Ozonation Trial Run	69
27	Biofilter Pilot Plant Suspended Solids Before and During Ozonation Trial Run (Sample Point 4)	70

LIST OF FIGURES, Continued

Figure Number	Title	Page
28	Biofilter Pilot Plant Suspended Solids Before and During Ozonation Trial Run (Sample Point 2)	71
29	Biofilter Pilot Plant Biochemical Oxygen Demand Before and During Continous Ozonation Trial Run	72
30	Dissolved Nitrogen During Air Feed Gas Continuous Run	73
31	First Gill Arch After 20 Minute Exposure to 0.3 mg/l Ozone	74
32	First Gill Arch After 7 Minute Exposure to 0.3 mg/l Ozone	75
33	Preliminary Suggested Design-Ozone Treatment System 650 GPM	76

LIST OF TABLES

TABLE NUMBER	TITLE	PAGE
I	Welsbach Ozone Generator Calibration Data	78
II	Grace Ozone Generator Calibration Data	80
III	Preliminary Laboratory Tests for Bacteria Survival	81
IV	Laboratory Determined Ozone Decay Concentrations for Half Life Calculation	82
V	Dilution Tests for Destruction of Residual Ozone	85
VI	Total Bacteria Plate Counts During Continuous Ozonation - Average of Three Plates	86
VII	Millipore total Bacteria Counts Taken During Continuous Ozonation	87
VIII	Pilot Plant, Startup and Approach to Steady State Before Ozone, Intermittent Ozonation Trial Runs and Continuous Ozonation Run	88
IX	Percent Dissolved Nitrogen Concentration	95
X	Continuous Run Contact Column Residual Ozone Delivered to Clarifier	96
XI	Continuous Run Residual Ozone - Column Out	99

ABSTRACT

An ozone pilot plant was installed at the Dworshak National Fish Hatchery to examine the efficacy of sterilizing makeup water entering this recycle hatchery. The pilot plant actually consisted of two separate systems operated together. A recycle system consisting of two fish tanks, a clarifier and biofilter was in operation prior to this study. An ozone system consisting of a Grace ozone generator (later replaced by a Welsbach generator) and a Grace contacting column was installed for this study. The ozone pilot plant supplied the makeup water to the existing recycle system. The pilot plant was run with approximately 125 pounds of cutthroat and one-half pound of steelhed fry. Recycle rate was 30 GPM and makeup rate was 3 GPM.

Plate counts for total bacteria were taken daily from various points in the pilot plant during a continuous (24 hours/day) two week run. Similar plate counts were taken from existing ultraviolet sterilization equipment. Also monitored during the continuous test run were ozone residual levels into and in the recycle system, ammonia, nitrate, nitrite, total organic nitrogen, suspended solids, turbidity and biochemical oxygen demand.

Analysis of the plate counts showed the ozone consistently provided better sterilization of the makeup water than the exisiting ultraviolet system. Ammonia levels with ozone sterilization showed a 70 percent decrease while

nitrate levels showed a 100 percent increase. Nitrite levels remained unchanged. Total organic nitrogen showed a 150 percent increase.

The recycle system was then altered to run 10 percent of the recycle water through the ozone pilot plant. This was done to determine if recycle water could be sterilized and if a general decrease of bacteria in the system could be realized. Process control problems with residual ozone levels caused shutdown after only four days of operation. However, enough data was collected to show that recycle water could be sterilized.

A trial was undertaken to determine the effect of an accidental ozone overdose on the fish in an actual operating system. Thirty percent of the recycle water was dosed with a 3 mg/l residual ozone level for five days in an effort to build up a residual in the system. No residual appeared in the fish tanks after this time indicating the system can tolerate a large accident without fish mortality.

Batch studies were also done on algae growths removed from the hatchery biofilters. These algae growths are so extensive on the biofilters they impair their operation. The batch studies indicated that ozone can effectively destroy algae. Retention times and dosage levels were not determined.

At the conclusion of the pilot plant study, an economic comparison was made of an ozone system and an ultraviolet system. The basis for comparison was a proposed 650 GPM

system to be installed at Dworshak. Although the ozone treatment system requires a capital investment of $164,000 as opposed to $90,000 for an equivalent size ultraviolet system and an annual cost of almost $17,000 as opposed to $12,000 for the UV system, this study demonstrates the increased cost may be justified. The ozone system gave consistently greater sterilization efficiency than the ultraviolet system. It also showed consistently lower ammonia level and more uniform BOD concentrations. All of these effects would enhance fish survival.

In addition, to these measured benefits algae destruction was demonstrated. This would result in a lower algae growth rate in the system and enhanced biofilter efficiency. This would also decrease ammonia levels and increase fish survival.

INTRODUCTION

The Dworshak National Fish Hatchery at Orofino, Idaho, is a recirculation type hatchery. Rearing pond water is treated in biofilters, filtered, aerated and recirculated back through the rearing ponds. A 10 percent portion of the recirculation water is bled off and fresh makeup water added to provide constant flow. The makeup water is presently being treated by filtration with sand filters and sterilization with ultraviolet lights.

Many problem areas exist in the hatchery which could be related to the exising makeup water system. These include:

(1) Algal blooms on the biofilter and in rearing ponds.

(2) Periodic infestation of fish pathogenic protozoans and bacteria.

The ultraviolet light system does not destroy algae entering the fish hatchery in the makeup water. In fact, it may actually promote algae growth. Figure 1 shows a length of ultraviolet light tube removed during periodic maintenance. The tube is completely covered with an algal growth. During high algae growth rate periods, cleaning of these tubes presents a maintenance problem. If the tubes are not cleaned they become covered with algae and "scum" and their sterilization action on bacteria and viruses is drastically reduced. These ultraviolet tubes also present a problem in

that they must be replaced twice a year. This is an expensive, time consuming project involving several hundred tubes and takes personnel from other required work.

The effect of ultraviolet lights on protozoans is not known. These continuing problems have led to the search for a better method of treating the makeup water. A treatment which will completely sterilize the water including protozoans and algae is desired. Ozone treatment in makeup water is the method being evaluated in this study.

Ozone is the second most powerful oxidizing agent known. It is currently in general use in Europe for treatment of potable water. It is starting to come into widespread use in the United States for tertiary treatment of waste water. Unlike chlorine, ozone breaks down naturally with a half-life of 15 minutes[1] to free oxygen. This release of oxygen enhances the water quality rather than leaving a harmful residual. Ozone has also been shown to reduce turbidity, color and odor of water.[2]

Many researchers have studied the properties of ozone in aqueous solution and its effects on various organisms.[1,3,4] A summary of their results indicates ozone is lethal to an average of greater than 96 percent of the test bacteria and virus in less than five minutes contact time and with a

residual concentration of less than 0.1 mg/l. Giese and Christensen[5] have shown that ozone is lethal to some protozoans in four minutes while others survived for as long as two hours. All protozoans showed signs of damage in a short time. Whether this damage is sufficient to prevent reproduction, is not known. The effect of ozone on algae is unknown, however, Homan[6] has shown that plant life is adversely affected by ozone in the air. The plants showed bleaching and wilting. It is possible that algae will show adverse affects from contact with aqueous zone solutions.

Few studies have been done to determine the affects of ozone on hatchery recirculation systems or fish. Rosenlund[7] reported in a study at Whiteriver, Arizona, that a residual ozone concentration as small as .01 mg/l produced 100 percent mortality of rainbow trout in four hours. Ozone has also been in continuous use for over one year as primary treatment in a recycle oceanarium in Orlando, Florida.[8] The oceanarium system is entirely closed with no bleed off and makeup is only for leakage and evaporation. The marine mammals and fish have shown no detrimental effects from ozone. BOD levels and bacterial level in this system have remained quite low.

The Fish and Wildlife Branch of the Department of Recreation and Conservation of Canada contracted a study[9] to evaluate the use of ozone as makeup water treatment in a

proposed fish hatchery. This proposed hatchery, the Abbotsford Hatchery, is similar in design to the Dworshak Hatchery. It is a recycle hatchery with a constant bleed and makeup of water. Unlike Dworshak, the makeup water is obtained from deep wells. The study consisted of using a Grace Ozone Generator and Grace Contacting Column identical to the ones used for this study. Water was ozonated, mixed with well water to obtain the same dilution as the proposed hatchery, passed through egg baskets and then fish rearing troughs, and released to a nearby creek. This study showed that a sterilization of bacteria of 99.6 percent was normal and that the fish were not harmed. It also demonstrated that any residual ozone was completely destroyed when the ozonized water was mixed with recycle water in a ratio of 1:4. Mortality studies were also run showing that a residual ozone concentration of .01 mg/l caused a 35 percent mortality in 195 minutes.

The primary objective of this study was to operate an ozone test unit to treat the makeup water of a recycle pilot plant. The pilot plant was operated on a recycle basis with clarification of recycle water and ammonia removal by biofilters. Makeup rate was 10 percent and from the North Fork of the Clearwater River, the same as the full scale system at Dworshak. the pilot plant used five to ten inch cutthroat trout in one fish tank to provide the loading and steelhead fry in another tank.

The study was run in this manner to test the effects of ozone on an actual operating recycle system. It is important to run the study in actual hatchery water because the rate of reaction of ozone varies with the quality of the water. As organic and inorganic contaiminants in the water increase, more ozone will be consumed in oxidizing these contaminants. Less ozone will remain for sterilization. It is important, then, to determine degree of sterilization in actual hatchery water.

Factors examined during the pilot plant trials are as listed below.

1. Sterilizability of river water by ozone on a continuous basis.
2. Determination of residual level ozone required for sterilization.
3. Ease of operation of an ozone system on a continuous basis.
4. Control of residual levels, in makeup water and in pilot plant system.
5. Effects on nitrifying bacteria.
6. Effects on fish--especially steelhead fry.

On completion of the makeup water treatment run, the system was altered for treatment of part of the recycle stream. The same parameters were then examined.

On completion of the recycle trial a study was run to determine how large an ozone residual can be tolerated without fish mortalities. Also secondary effects of of an ozone accident were determined.

Prior to the pilot plant work, laboratory studies were completed to determine rate of decay of ozone in hatchery water. Also studied in the laboratory were the affects of ozone on algae, and the efficacy of ozone as a sterilant.

After completion of the above studies, an economic analysis was made. The analysis determined the capital and operating costs of an ozone treatment system. The system design is based on data collected above. Finally, the cost of an ultraviolet treatment system of equivalent size was compared to the ozone system.

ANALYTICAL PROCEDURES

1. Bacteriological Examination:

Bacteriological studies were carried out by plate count. Disposable presterilized petri dishes were used with a media of commercial Trypticase Soy agar. The agar was prepared for pouring into the petri dishes by the following method.

> Mix 40 grams powder Trypticase Soy agar with one liter of distilled water in a suitable flask. Cover with aluminium foil and place in an autoclave for twenty minutes at 15 PSIG. After autoclaving and before cooling, place flask in a constant temperature bath at 55 degrees C. When agar starts to thicken pour into petri dishes. Flame mouth of flask frequently during pouring. Pour as per Standard Methods.[10]

After pouring, the petri dishes were stored at room temperature overnight then placed in a refrigerator for storage until use. While in the refrigerator the petri dishes were inverted and covered to prevent contamination.

Sampling

The method of sampling for bacterial counts was determined in conjunction with the University of Idaho Bacteriology Department[11] and is as follows:

If the sample is from a sample valve, open valve and allow to flush for one minute. If the sample is from a tank, a grab sample is taken. A sterile test tube is rinsed once with sample water then filled. A sterile 1/10 ml/inch pipette is used to withdraw sample from the test tube. One-tenth ml of sample is placed on each of three

petri dishes. The sample is spread evenly over the agar surface using a sterile "hockey stick." Care must be used not to tear the surface of the agar.

The plates were incubated for three days at room temperature. During incubation to prevent overgrowth of colonies in the more contaminated samples and yet allowed detection in the less contaminated samples, the plates were inverted, covered and kept from drafts. The results were multiplied by ten to obtain bacteria per millimeter.

2. Ozone in Gas

During the laboratory work calibration of the ozone generators required a method for determining concentration of ozone in gas. Ozone in oxygen was determined by the standard iodometric method. For this test the ozone containing gas was passed into a washing bottle containing one liter of 0.1N KI solution. A second washing bottle containing KI was connected in series with the first bottle to insure all ozone was absorbed. The gas discharge volume was measured by a wet test meter. After ozonation, the KI solution was placed in 2,000 ml beaker. The washing bottle was rinsed with distilled water and the rinse water added to the beaker. The sample was then titrated using standardized sodium thiosulfate and starch. See Appendix C for sample calculation of ozone concentration in gas.

3. Ozone Dissolved in Water:

A method for measuring ozone dissolved in water was adopted from "Pilot Plant Tertiary treatment of Wastewater with Ozone."[12] This method is as follows:

Add 80 ml of 0.1N KI and 1 ml of .05N KOH to a 500 ml beaker. Fill beaker to 480 ml with ozonated sample. Place beaker on a magnetic stirrer and while stirring add 20 ml. 0.1N sulfuric acid . Titrate with standardized sodium thiosulfate and starch.

4. The following Analysis was Done As Per Standard Methods Techniques:

Nitrates in solution (Brucine method)

Nitrites in solution

Ammonia in solution (Nesslerization method)

Biochemical oxygen demand

Total organic nitrogen (Kjeldahl method)

Alkalinity

Dissolved oxygen

Suspended solids

These samples were taken at Dworshak, placed on ice and returned to University of Idaho for analysis on same day.

5. Turbidity:

Turbidity of water was determined using a HACH Model No. 2100A turbidimeter which reads directly in Jackson turbidity units.

6. pH:

pH levels were determined using three different pH meters. First, a Corning Model 610A portable pH meter was used. Subsequent problems caused replacement with a Markson Model 80 digital pH meter. This meter was found to be inaccurate outside of a small band around pH of 7.0. This meter was replaced with a Beckman Zeromatic SS-3. This stopped working after several days. pH was not measured in the field after this.

7. Dissolved Nitrogen in Solution:

Dissolved nitrogen gas was determined using a Weiss Saturometer Model No. ES-2

8. General:

It was also desired to find a method of measuring dissolved ozone which was readily adaptable to field work. This method would then be tried in the field and if successful, would be recommended as useful in a full scale system. In this context the Schechter method[13] was evaluated. After laboratory trials it was decided not to use this method in the field. There were several reasons for this. First, and most important, was that turbidity in the water caused inaccuracies in the results. A waiting time of 30 minutes, to allow color development in the sample was also considered unsatisfactory for field work. This method was however used in the laboratory and gave very accurate results within certain limits.

The second method evaluated was the Orthotolidine Manganese-Sulfate Method (OTM)[10] for residual ozone. This method involves use of a chlorine color comparator to find residual "chlorine" level. This is then divided by 1.45 to give residual zone. This method was found to be less accurate than the Iodometric or Schechter techniques. It is, however, very rapid in that results can be obtained within one minute of sampling. This method has been in satisfactory use at the Whiting, Indiana Potable Water Treatment Plant for many years. It has one major drawback. The chemical Orthotolidine (4,4'-diamino-3,3'-dimethyl-biphenyl) is the primary reagent. This is a suspected carcinogen and must be handled with extreme caution.

For the majority of this study the Idometric technique was used, since it is slightly more accurate than the OTM technique. The OTM technique is limited by the color comparator accuracy. The Iodometric technique was difficult to use in the field in that daily standarization of the Sodium Thiosulfate was required. Also, several different chemicals (0.1N $Na_2S_2O_3$, 0.01 $Na_2S_2O_3$, KOH, 0.1N H_2SO_4 Conc. H_2SO_4, 0.1N KI) were required and much (somewhat cumbersome) glassware which needed constant cleaning and rinsing with distilled water was required. Once these nuisance type problems were worked out, the Iodometric technique was satisfactory.

EQUIPMENT DESCRIPTIONS

Numerous equipment was used during this study. A list and description of important pieces is given below, along with appropriate comments. Also included is a description of the pilot plants and their daily operating requirements and sample points.

Grace Ozone Generator Model LG-2-L2: (air cooled, gas flow 10 to 100 SCFH).

This ozone generator was used extensively during the laboratory studies. However, early in the continuous pilot plant run it experienced a major failure. Replacement of electronic components failed to repair the generator. The Union Carbide Company, the manufacturer, was contacted and it was established that warping of the Lowther tube had occurred. This repair took over a week to accomplish and the unit was not placed back in continuous service during the rest of the trial. It was, however, used as a back up unit.

Welsbach Ozone Generator Model Cl-D: (water cooled)

This older model Welsbach unit was recovered from a previous installation[2] and rebuilt as a single unit. Even though this unit is simpler in construction than the Grace unit, in that it does not use high frequency current, it produced a higher ozone concentration in the gas (Figure 4). It was used as the primary unit during the continuous pilot plant run and operated continuously for two weeks with no maintenance.

Constant Voltage Source:

To prevent voltage fluctuations from affecting the ozone concentration, constant voltage transformers were connected between the ozone generator and the power source.

Contact Column:

A Grace experimental contacting system was used to contact the ozone into the raw water. This column is shown in Figure 10. The actual method of mixing is Grace proprietary information, but the column, after mixing, consisted of three concentric pipes. The gas, dispersed in liquid mixture, passes down the innermost column, up the middle column and down the outer column. Residence time can be varied by varying the level in the outer column. For this study a standpipe was used which kept the outer column full. A sample valve was installed on the standpipe which allowed sampling at the column outlet.

Prior to the continous run, a test was made to determine overall efficiency of the contact column. For this test the gas washing bottle was connected to the vent of the contact column. The generator was preset to a calibrated concentration and residual out of the column was measured. The concentration in the vent gas was also measured. The test showed that at 3 GPM and 20 SCFH the water was only absorbing about 61 percent of the delivered ozone. The low efficiency probably comes from the low flow rate of liquid. Efficiency was not tested at higher flow rates since they were not pertinent to this study.

Wet Test Meter:

For volumetric measurement of gas, a Precision Scientific Wet Test Meter No. 63125 as used. This meter has a maximum flow rate of 24 Ft^3/Hr and a minimum flow rate of 2 Ft^3/Hr. It was used to calibrate the ozone generators.

Ozone Pilot Plant:

The ozone generating and contacting pilot plant consisted of the generator and contact column (see Figure 11). A header for connecting three gas cylinders to the generator supplied the gas. At the set flow of 20 SCFH the three cylinders supplied enough gas for 36 hours of continuous operation.

Once the plant was started for the continuous run it required very little actual attention. Daily operating instructions are listed below:

1. Check residual ozone concentration in makeup water. Adjust watts as necessary to obtain required residual.
2. Check for residual ozone in clarifier (see biofilter pilot plant), inlet and outlet.
3. Bacteria plate count samples (daily):
   Raw water (from sample line)
   Post UV (from incubator water)
   Post ozone (from sample line)
   Clarifier (grab sample)
4. Change gas cylinders

Biofilter Pilot Plant:

The biofilter pilot plant was in existence at Dworshak National Fish Hatchery for several years prior to this study. It was in use primarily by the University of Idaho Department of Civil Engineering for studying various types of media used to grow nitrifying bacteria. The plant was a self-contained recycle system designed to operate in the same manner as the hatchery.

A schematic diagram of the plant is shown in Figure 12. It consisted of:

(4)-500 gallon fiberglass tanks

(1)-biofilter tower--wooden 41" x 44" x 10 feet.

(1)-pump

Two of the fiberglass tanks were connected in parallel and were used as fish ponds. One contained one half pound of steelhead fry (at 500 to the pound). The other contained 150 pounds of cutthroat trout, which were primarily for loading on the biofilter.

The two fish tanks drained by gravity flow to another 500 gallon tank which was used as a clarifier. This tank was baffled to minimize short circuiting, and had an automatic sludge scraper. The sludge drained by gravity flow to a sludge basin. The supernatant liquid flowed out of the clarifer through a weir to the pump reservoir (the last 500 gallon tank). From the reservoir it was pumped to the bottom of the biofilter tower, and passed up through the

biofilter media and out to the fish tanks via a weir in the top of the tower. The biofilter media was Norton rings and provided a culture surface for nitrifying bacteria which oxidized ammonia to nitrates.

Total system volume was 3,000 gallons. Recirculation flow rate through the system was 30 GPM. Makeup water flow rate was 3 GPM. Bleed off, out of the pump reservoir by overflow, was also 3 GPM.

The cutthroat fish tank had automatic fish feeders connected above it. These feeders fed the cutthroat approximately 2.3 pound of 1/8" fish pellets per day. The steelhead fry were too small to be fed by automatic feeders and were fed on a daily basis by Dworshak operating personnel.

Daily operating instructions and sampling points are given below:

1. Sample procedure: (see Figure 12).

   Monday, Wednesday and Friday:

   2 liter sample at each of the following: biofilter outlet, fish tank outlet and settling tank outlet.

   1 liter sample, sludge basin.

   Friday:

   1 liter sample at base of biofilter.

2. Fish feeding:

   2.3 pounds fish food per day into automatic feeders.

   (steelhead fry fed by hand by Dworshak personnel)

3. Record on chart:
   sludge depth
   water temperature
   Pounds fish feed
4. Drain sludge basin
5. Clear all drain valves by opening momentarily
6. Visually inspect fish for mortality or signs of stress. The water samples were iced and removed to the University of Idaho for measurements as previously described.

Integrated Pilot Plant:

The pilot plants were combined and operated as a unit for the study. A schematic of the integrated system is shown in Figure 13. This was the system as operated with ozone treated makeup water. Figure 14 shows the integrated pilot plant as it was operated during the ozonation of recycle water.

LABORATORY STUDIES

Several laboratory studies were necessary before the integrated pilot plant run could begin. There were three objectives of these studies. First, to become familiar with the operation of the equipment and verify it was functional. Second, to find preliminary operating parameters. Third, to show that in a laboratory trial, the objectives of the integrated pilot plant run could be achieved. To this end, the laboratory studies included:

1. Verify and become familiar with a satisfactory method of ozone measurement.
2. Calibrate the equipment.
3. Show that sterilizaton can be achieved.
4. Develop an ozone decay model and use this to predict ozone residual from the pilot plant treated water outlet.
5. Predict the rate of decay of ozone residual in the pilot plant.
6. Show that dilution can eliminate residual ozone.
7. Show that algae growing in the fish hatchery biofilters is susceptible to destruction by ozone.

To accomplish the laboratory studies, the equipment was setup as shown in Figure 3. For discussion of individual pieces of equipment see previous section on equipment. Gas flow through the setup was as follows:

> Oxygen passed from the cylinder through a regulator to the ozone generator. From the generator the ozone and oxygen stream passed to the three-way valve. From here, it could either be vented to atmosphere or passed

to the gas washing bottles. During a trial, the generator was normally started and the product gas vented to atmosphere for one half hour to allow the generator to come to steady state. The valve was then reset to allow the gas to flow to the sample bottle, then to the potassium iodide trap and last to the wet test meter.

Ozone Measurement Techniques:

The first laboratory work was to verify and become familiar with methods for measuring ozone. These methods are discussed in the section on analytical methods, but are listed below for reference:

1. Iodometric - concentration in gas.
2. Iodometric - concentration in liquid.
3. Shechter analysis - concentration in liquid.
4. Orthotolidine Manganese-sulfate Method-concentration in liquid.

Unless otherwise stated, the Iodometric technique was used in the studies listed below.

Equipment Calibration:

After enough trial runs to become familiar with the analytical methods, calibration of the equipment was begun. It was felt that reproducibility of the methods, which have already been proven by other researchers, and equipment calibration could be carried out together.

The first calibration completed was the Grace ozone generator. At constant watts (150) gas flow through the generator was varied to produce a concentration in gas versus gas flow rate curve (see Figure 4). This was accom-

plished by ozonating a known volume of potassium iodide and measuring the gas volume in the wet test meter. This was done for six different flow rates. A similar calibration curve was then developed for the Welsbach unit (see Figure 4).

The curves, as worked out, were much closer than one would have suspected. This was an unexpected benefit because it meant the Welsbach unit which was the backup unit (and actually ended up as the primary unit) could be interchanged with the Grace unit with little change of operating parameters.

Preliminary Sterlization Studies:

After calibration of the ozone generating units, trial studies were begun to see if sterilization could actually be achieved. This work was done in conjunction with the University of Idaho Department of Bacteriology, which actually did the bacteriological plate counts. The analytical method for residual ozone used was the Shechter technique. The test bacteria chosen were Bacillus polymyxa spores, Aeromonas liquifaciens and Enteric Red Mouth (ERM), all in triple distilled water. B. polymyxas spore was chosen because of its toughness. It was felt that if significant destruction of these could be achieved, other bacteria would be more susceptible. A. liquifaciens and ERM were chosen because they are fish pathogens. Two runs were made using B. polymyxa spores (see Figure 5). The

results of these runs indicated a minimum of a 92.7 percent kill within five minutes of contact.

The A. liquifaciens trial (Figure 6) indicated a 97 percent kill could be achieved within one and one half minutes. The ERM run was even more encouraging, indicating total sterilization could be achieved in four minutes (see Appendix A Table III).

The laboratory trial runs were all very encouraging. They indicated that a significant kill could be achieved within the contact time in the pilot plant contact column. No attempt was made to determine a minimum ozone to sterilization model. It was felt ozone demand of fish hatchery water would make any attempt to find minimum laboratory ozone requirements of little value.

Ozone Decomposition Rate:

Once it was shown sterilization could be achieved in a reasonable time, it was desired to estimate initial parameters of operation of the pilot plant. To do this it was necessary to study the kinetics of ozone decomposition in actual Dworshak Fish Hatchery water. Makeup water, which had not been filtered or sterilized with ultraviolet light (UV) (hereafter referred to as raw water) was obtained from the Dworkshak National Hatchery for each experiment.

The method of approach to the problem of ozone decay kinetics was to find a decay rate model due to naturally occuring material in the water. During this laboratory

study, plate counts for total bacteria and BOD in raw water were also being done at Dworshak. These counts (see Appendix A Table VI) indicated that at the time of the year (April) bacteria concentrations and BOD were very low. Organic material was then considered negligible for ozone demand in the water, and the only demand was considered to be inorganic.

The raw water was ozonated for approximately one hour. The generator was then shutdown and samples withdrawn from the column for residual concentration determination. The samples were withdrawn directly into a KI solution (as outlined in the analytical section under, "Iodometric in Solution") to stop the reaction. Timing was, then, very accurate. The experiment was run four times, once for over four hours to determine as accurately as possibly the decay rate.

The trial results are summarized in Figure 7 showing different initial concentrations and measurement times. Kilpatrick,[14] et al, have shown the rate of decomposition of ozone in distilled water to be proportional to the 3/2 power. Even though this is a very good correlation it was decided not to use it for this study. Examination of Figure 7 shows that after an initial drop of approximately one third, the decomposition becomes linear on a log scale. It was decided for simplicity to assume that one third of the initial ozone is immediately destroyed and that the remaining

ozone decays with first order kinetics. The decay model then becomes (after the initial drop):

$$(1) \qquad [O_3] = [O_3]\, e^{-\lambda t}$$

Solution of equation (1) for a half life ($t_{1/2}$) using the data in Figure

$$t_{1/2} = 8 \text{ min.}$$

$$\lambda = 087/\text{min.}$$

This half life is significantly less than for ozone in distilled water, which is approximately 15 minutes.[1] This indicates there are inorganics in the water which are probably catalyzing the ozone decomposition.

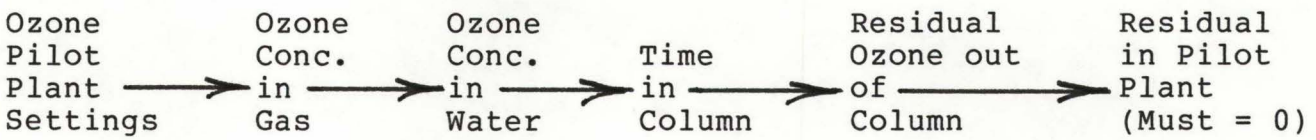
Estimation of Pilot Plant Operating Parameters:

With the rate of decay of ozone in raw water determined, the next step was to find the rate of transfer of ozone into the water. This is a much more difficult problem. The method of contacting and rate of decomposition both affect the rate of mass transfer.

Rawson[15] has done an excellent study on the uptake of ozone by water. To simplify the problem several assumptions were made. This allowed the use of Rawson's rate curves for finding ozone uptake from the gas. The assumption was that the method of contacting was similar to that of Rawson, namely a diffuser in a stagnant tank. It was realized that this was a gross assumption, but it was hoped that an order of magnitude figure might be found. Then after the

pilot plant was running this might be refined.

The only piece of laboratory information missing was the concentration of ozone at the outlet of the ozone column. If this was known the following scheme would be complete:



With a residual ozone concentration out of the ozone pilot plant known, an initial ozone concentration in the water can be calculated. Using Rawson's data a concentration of ozone in gas can be found and from the calibration curves initial settings of the pilot plant can be determined.

The requirements for ozone concentration out of the column were that it be sufficient to insure sterilization, but low enough to be destroyed by dilution in the overall pilot plant. A previous study[9] showed that if water with a residual ozone concentration were diluted 1:4 with raw water then all measurable ozone is decomposed. It was decided to try this method in batch tests using hatchery water. The test was made using two different sources of water from the hatchery, and at several different dilutions. Clarifier water, from the pilot plant, decomposed the ozone as the British Columbia study[9] predicted. Raw water, however, required a dilution of 1:20 before residual ozone could no longer be measured (see Table V). This indicates it is

probably not the mechanism of dilution, but the introduction of an ozone demand that decomposes the ozone.

It was desired to run the integrated pilot plant as close as possible to the parameters of the actual hatchery. The recycle rate of the pilot plant was fixed at 30 GPM. Since the hatchery operates at 10 percent makeup, the makeup of the pilot plant was also set to 10 percent or 3 GPM. The makeup was to be introduced into the clarifier, a 500 gallon tank. The British Columbia study and this study's verification showed that at this rate any measurable residual would be destroyed. It was then decided to use 1 mg/l residual ozone out of the column. This was high enough to insure sterilization, yet low enough to be decomposed in the clarifier.

The initial parameters of the pilot plant were then calculated (see Appendix D for sample calculation) using the method previously outlined. The results are listed below:

water flow rate: 3 GPM

oxygen flow rate: 20 SCFH

The calculated gas flow rate had more than one reason for being used. The ozone generator gas feed was from a header with three, 204 standard cubic feed tanks connected to it. If the feed rate was 20 standard cubic feet per hour, two tanks would be used for 24-hour period leaving a one half safety margin. It was decided to use this gas flow rate as a constant. If reduction of ozone concentration was desired,

it was decided to lower the watts, or volts, as required. If required, further calibration curves would be generated as needed.

Ozonation of Algae:

With the completion of the pilot plant parameter estimation only one laboratory study was left. It was desired to find the affect of ozone on algae growths. This was to be a batch study with no attempt to find kill rates versus concentration of ozone. It was only desired to find whether or not ozone will destroy algae in a reasonable time. To do this, a trip was made to Dworshak and five gallons of biofilter water with a large amount of algae in it was obtained and transported immediately to the University. Approximately one and one half liter of this water was placed in a gas washing bottle. The ozone was then turned on and allowed to pass through the sample. Ozone flow rate and concentration was not determined, because it was necessary to change flow rates down during the run, due to foaming. Immediate change was noted on the algae. Foaming and color change were noted within two minutes. At the end of fourteen minutes no green color remained in the algae. Observation under a microscope prior to ozonation identified one of the species as Spirogyra. The other observed was not identified. Inspection of the water under a microscope after ozonation showed the cell walls to be intact.

However, all chlorophyll was bleached colorless. The majority of the cells had only the walls remaining. The insides being completely empty. Some cells in the centers of large clumps showed some chlorophyll remaining. This was, however, broken up into small clumps and not in a continuous chain as is typical of food storage in Spirogyra. Figure 8 shows the affects of ozone on the algae at various times during the ozonation. At the completion, fourteen minutes, no solid colored material remained.

A control study was also done using oxygen (see Figure 9). this was run to insure that it was not the physical action of gas bubbles passing rapidly through the sample that destroyed the algae. At the end of fourteen minutes, no change in the algae was noted with oxygen only. No foaming occurred during the oxygenation. It was concluded that the destruction of the algae was not due to physical mixing.

PILOT PLANT STUDIES

Original Plan:

The integrated pilot plant study at Dworshak was divided into several distinct segments. The original plan was to ozonate the makeup water for one month, two weeks using oxygen as the feed gas to the ozone generators and two weeks using air as the feed gas. Air was to be used for two weeks to check for nitrogen supersaturation. Nitrogen supersaturation is a continuing problem at Dworshak and it was required to determine if the ozone contact system would contribute to it. Also, it was necessary to show that nitrogen compounds harmful to fish were not produced during ozone generation with air.

On completion of the makeup water run, it was planned to realign the ozone contacting system to treat a partial flow of the recycle water. The reason for this was to determine if sterilization of the recycle water could be achieved. A continuous run of two weeks on recycle was originally planned.

Another parameter required for scaleup of the pilot plant results was the extent of an ozone overdose which could be tolerated in the system before fish fatalities resulted. To determine this, a large amount of residual ozone would be introduced into the recycle water. The residual ozone in the system would then be monitored. The test would be timed

from startup of the ozone excursion until fish fatalities occurred.

Preliminary Trials:

Prior to startup of the pilot plant for a continuous run, several one day runs were made to check for residual ozone levels. For these runs, raw water was ozonated in the contact column then passed to the sewer. Residual levels leaving the contact column were measured at various water flow rates, gas flow rates, and power levels. Measured values are shown in Figure 15. It should be noted that for 10 GPM water flow, residual ozone concentration decreases with increasing gas flow rate. However, at 20 GPM, residual first increases, then decreases with increasing gas flow rate. This phenomenon, along with the alternating slopes of the curves indicates a complex mechanism occurring in the column.

Prior to ozonation of the biofilter pilot plant, fifteen of the steelhead fry were dissected for gill studies. Photographs of the fish gills are shown in Figure 16. It should be noted that some edema and "clubbing" of the lamellae was present. These fish were examined by the resident fish biologist at Dworshak who determined they were normal recycle hatchery fish.

A complete chronological account of the continuous pilot plant operation and reasons for changes in schedule is

detailed in Appendix B. Table X details the conditions of the ozone generator and dissovled ozone concentrations during the continuous run.

To summarize the study, a two week run of continuous ozonation of makeup water was successfully completed. This consisted of one week of oxygen as feed gas to the ozone generator and one week of air as the feed gas. The pilot plant was then realigned to treat 10 percent of the recycle water flow (see Figure 14). Difficulty in attaining a steady state condition of residual ozone out of the treatment column caused termination of this experiment after three days. The accidential ozone excursion experiment was then run for three days. At the conclusion of this experiment, the pilot plant was dismantled and returned to the University of Idaho.

PILOT PLANT RESULTS

Results of data collected during the continuous ozonation run are shown graphically in Figures 18 through 30. Figures 31 and 32 show the affects of ozone on the first gill arch of fish killed by ozone in the mortality study. Each figure, or group of figures is discussed separately below.

Figures 18 and 19: These are comparison points of millipore total bacteria counters and plate counts of the makeup water after sterilization. Variation between millipore and plate counts suggest that the millipore counters are not accurate enough for scientific research. They are sufficient, however, to show approximate sterilization efficiency. In an operating fish hatchery, millipore counters are a fast convenient method to show extent of sterilization.

Figure 20: This shows ozone, UV and raw water bacteria levels. The ultraviolet sterilizers lower the bacteria level in the water. Ozone sterilization lowers the level of bacteria by a factor of three to ten more than the ultraviolet sterilization.

Figures 21, 22 and 23: These figures show nitrite, ammonia and nitrate levels in the fish tanks. During the continuous run, ammonia levels are lower than the run without ozone. Nitrate levels are higher during the ozone run. Nitrite levels are not significantly affected.

Figure 24: Total organic nitrogen is slightly increased during the ozone run.

Figure 25: Biochemical oxygen demand shows no significant increase or decrease. There does appear to be somewhat of a leveling affect during the ozone run.

Figure 26: Ozone concentration in the system has no affect on alkalinity.

Figure 29: In the above figures only one or two sample points are plotted out of the three sample points taken. Usually sample point four is used because this was the inlet to the fish tanks and, therefore, most significant. Figure 29 shows BOD plotted for the three sample points. It indicates that even though there is some variation the trend of all the points is the same, and reporting one point shows trends in the system at all points.

Figure 30: The points gathered are limited but do show nitrogen supersaturation above that which is already in the water (air used to generate ozone rather than oxygen).

Figures 31 and 32: These figures show the action of ozone on the fish gills. Severe edema and desquamation of eipithelium is apparent in both figures. This level of ozone in the fish tank (0.3 mg/l) was sufficient to attack and destroy the epithelium of the lamellae.

The fish killed during the mortality study were histologically examined to determine if ozone caused other

changes than on gill tissue. Tissues examined were heart, liver, gill, kidney and gastrointestinal tract.

The gills showed, as mentioned above, severe degeneration. Death was most probably from osmoregulatory failure.

Livers showed congestion and mild diffuse necrosis of liver cells. Kidneys showed mild necrosis of tubule epithelial cells and tubule lumens contained large quantities of proteinaceaus material. The pyloric caeca and intestine showed necrosis of the mucossa and submucosa. Heart muscle was stringy and pale staining with mild necrosis of muscle cells in the outer cortical layer.[17]

COST OF OZONE STERILIZATION

Analysis of an ozone system to treat 650 GPM of makeup water at Dworshak National Fish Hatchery is shown in Figure 33 and detailed in Appendix E. Estimated capital cost for the system is $164,000 and total annual cost is estimatd at approximately $17,000/year. Capital cost for an ultraviolet system is approximately $90,000 and annual cost estimated at $12,000/year. Details are given in Appendix F.

Ozone does a significantly better job of makeup water sterilizaton than ultraviolet light. In doing so it may enhance the operation of other parts of the system. It is difficult to assign a dollar value to these indirect benefits, but they should be considered.

CONCLUSION

Ozone is a better sterilant for treatment of Dworshak River water than is the existing ultraviolet light system. In addition to destroying significantly more bacteria, ozone can destroy algae which ultraviolet sterilization does not. Destruction of incoming algae in the makeup water could have a profound effect on the system. Most important, biofilter action could be enhanced causing a general decrease of stress on the fish.

Other affects of ozone sterilization of the makeup on the water in the recycle loop are decreased ammonia levels, increased nitrates and increased total organic nitrogen. Biochemical oxygen demand (BOD_5) is also somewhat steadier during ozone sterilization of the makeup.

Decreased ammonia and increased nitrates indicate the activity of the nitrifying bacteria somehow enhanced. Increased total organic nitrogen may be caused by the action of residual ozone leaching organic solids. This leaching would prevent the continuous buildup, and sudden discharge of organic nitrogen into the system, a common occurrence in biological systems. In other words, the level of total organic nitrogen would be steadier, decreasing stress on fish. A steadier BOD_5 level would also lessen stress on the fish.

The above actions of ozone on the system may not be the direct result of ozone. Rather, it may be some indirect affects such as decreased algae causing enhanced nitrifier action.

Ozone treatment of the makeup water is a stable, easily operated method of sterilization. The ozone residual control generally requires little or no adjustment. Methods of determining residual ozone levels are simple, rapid and accurate. In addition, should an accidental overdose of ozone enter the system, several warnings occur before the levels become harmful to the fish. Ammonia and nitrate levels increase drastically. This is due to destruction of the nitrifying bacteria in the system by ozone. Ozone levels can be rapidly changed as soon as high ozone residual level is determined. This study also determined that steelhead fry and cutthroat can be exposed to 0.1 mg/l ozone for as long as two days and show no signs of stress. To introduce this level into a full size hatchery system would require a drastic accident.

As a treatment for recycle water, ozone can definitely sterilize the water. There are, however, several problems that indicate further study is required. A steady state concentration of ozone was never achieved during this part of the study. This was probably due to changing water quality, typical of a biological system. Further study is

required to determine the control characteristics of applying ozone to the recycle flow.

During the two and one half weeks of continuous 24-hour per day operation and in spite of two overdose accidents, no fish mortalities occurred. For approximately 20 hours per day the pilot plant was unattended. In addition, at the conclusion of the study the fish showed no signs of greater stress than at the beginning of the study.

During this study there was no detectable ozone odor in the incubator room. This indicates that at the levels required for sterilization, there is no hazard to operating personnel. During short term high ozone concentration trials, ozone odor was detectable in the room. For this reason it is recommended that an air monitor be used on any ozone system.

An ozone system is significantly higher in installation and annual cost but may be more than justified by the general improvement of the recycle system.

RECOMMENDATION

Based on the improved performance of ozone over ultraviolet light sterilization, it is recommended that an ozone system be installed to treat water for the proposed System IV at Dworshak. Using System IV, a long term study of the benefits or deficits of ozone treatment can be made. From this information it would be possible to determine if ozone treatment should replace all of the ultraviolet treatment.

BIBLIOGRAPHY

1. Evans, F. L., Ozone in Water and Wastewater Treatment, Ann Arbor Science Publishers, Inc., Ann Arbor, Mich., 1972.

2. Harding, H. L., Development of a Portable Ozone Test Unit, Masters Thesis, University of Idaho, 1971.

3. Rice, R. G., Browning, M. E., Ozone for Water and Wastewater Treatment, International Ozone Inst., Waterbury, Conn., 1975.

4. Rice, R. G., Blogoslawski, W. J., Aquatic Applications of Ozone, International Ozone Inst., Waterbury, Conn., 1975.

5. Giese, A. C., Christensen, E., "Effects of Ozone on Organisms," Physiological Zoology, Vol. XXVII, No. 2, April 1954.

6. Homan, C., "Effect of Ionized Air and Ozone on Plants," Plant Physiol., p. 975-78, vol. 12, 1937.

7. Rosenlund, B. D., "Disinfection of Hatchery Water Influents by Ozonation and the Affects of Ozonated Water on Rainbow Trout," Aquatic Applications of Ozone, p. 59-66, International Ozone Institute, Waterbury, Conn., 1975.

8. Murphy, W. K., "The Use of Ozone in Recycled Oceanarium Water," Aquatic Applications of Ozone, p. 87-93, International Ozone Institute, Waterbury, Conn., 1975.

9. Sparrow, R. A., Fish and Wildlife Branch, Dept. of Recreation and Conservation, Victoria British Columbia, Personal Communications.

10. "Standard Methods for the Examination of Water and Waste Water," 13th ed., APHA, AWWA, WPCT, New York (1971).

11. Personal conversation with Patricia Colberg, Graduate Student, University of Idaho and Dr. A. J. Lingg, Associate Professor of Bacteriology, University of Idaho Department of Bacteriology.

12. Wynn, Clayton S., et al., "Pilot Plant for Tertiary Treatment of Wastewater with Ozone," Superintendent of Documents, U.S. Government Printing Office, Washington. D.C. Document No. EPA-22-73-146, 1973.

13. Shechter, Hana, "Spectrophotometric Method for Determination of Ozone in Aqueous Solutions," Water Research, p. 729-739, Pergamon Press, London, 1973.

14. Kilpatrick, M. O., Herrick, C. C., Kilpatrick, The Decomposition of Ozone in Aqueous Solution, American Chemical Society, p. 1784-1789, vol. 78, May 5, 1956.

15. Rawson, A. E., "Studies in Ozonisation," Water and Engineering, March, 1953.

16. Veloz, Thomas, Aquafine Corp., Burbank, Calif., Personal Communication.

17. Smith, C. E., Hatchery Biologist, Fish Cultural Development Center, Bozeman, Montana, Personal Communication, September 3, 1976.

18. Rosen, H., Burhans and Sharpe Co., Seattle, Wash., Personal Communication.

19. McEthreon, L., Orbit Industries, Washougal Wash., Personal Communication.

20. Hacker, R., Archer Blower and Pipe Co., Portland, Oregon, Personal Communication.

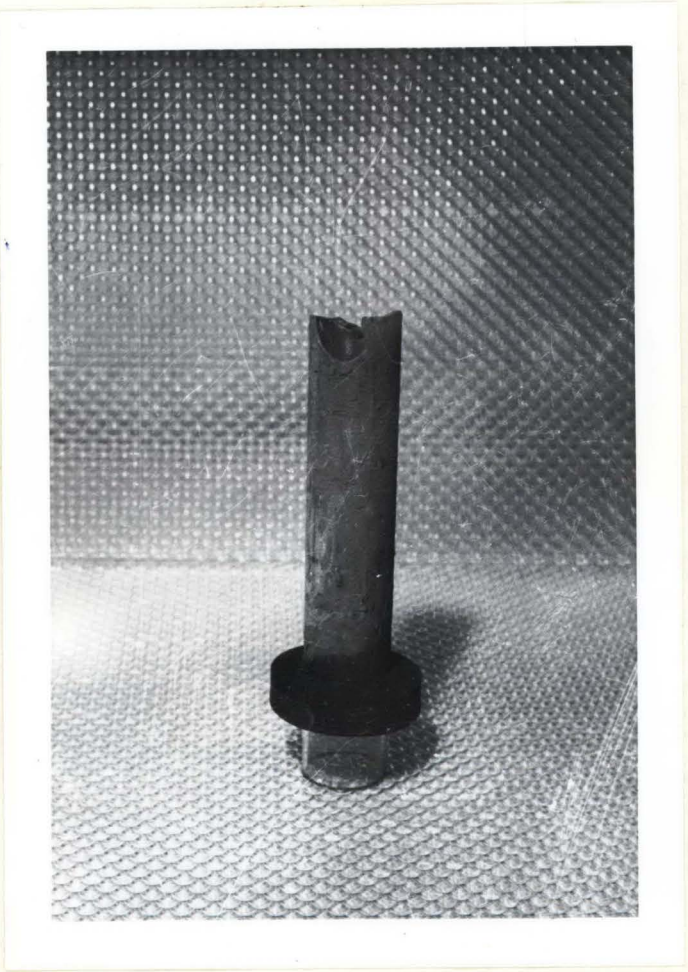


Figure 1
Algae Growth on Ultraviolet Light Sterilizer
at Dworshak National Fish Hatchery
During Peak Algae Growth Period - Spring

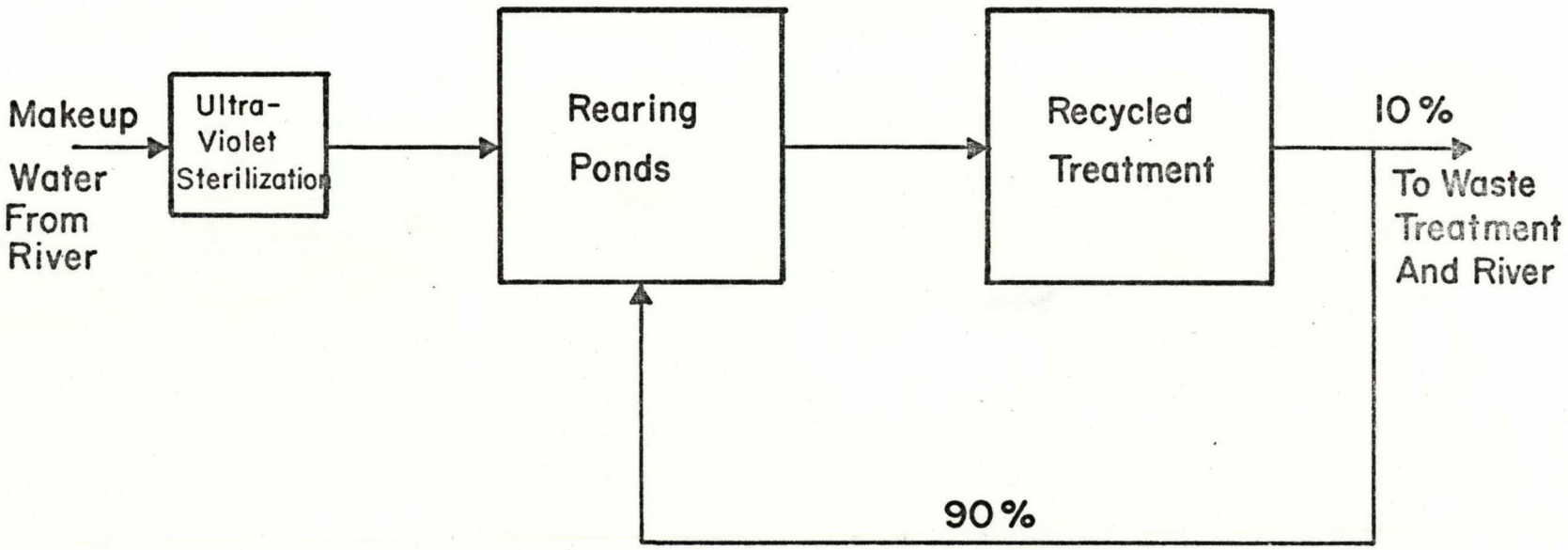


Figure 2. Water Flow Schematic, Dworshak National Fish Hatchery

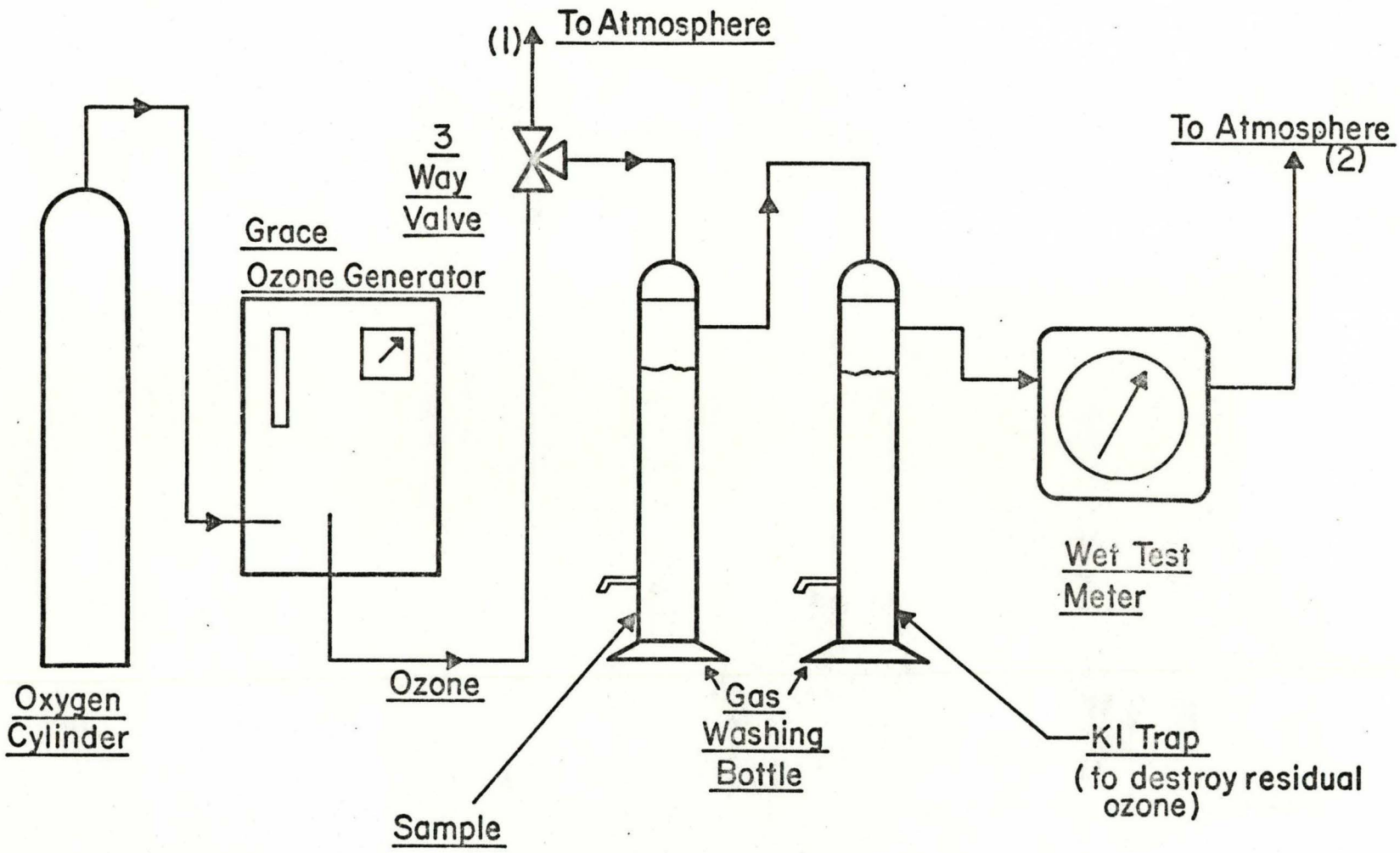


Figure 3. Laboratory Apparatus For Ozone Treatment

FIGURE 4

Calibration Curves for
Ozone Generators

Welsbach Grace

115 Volts 200 Watts

(Corrected to Standard Pressure and Temperature)

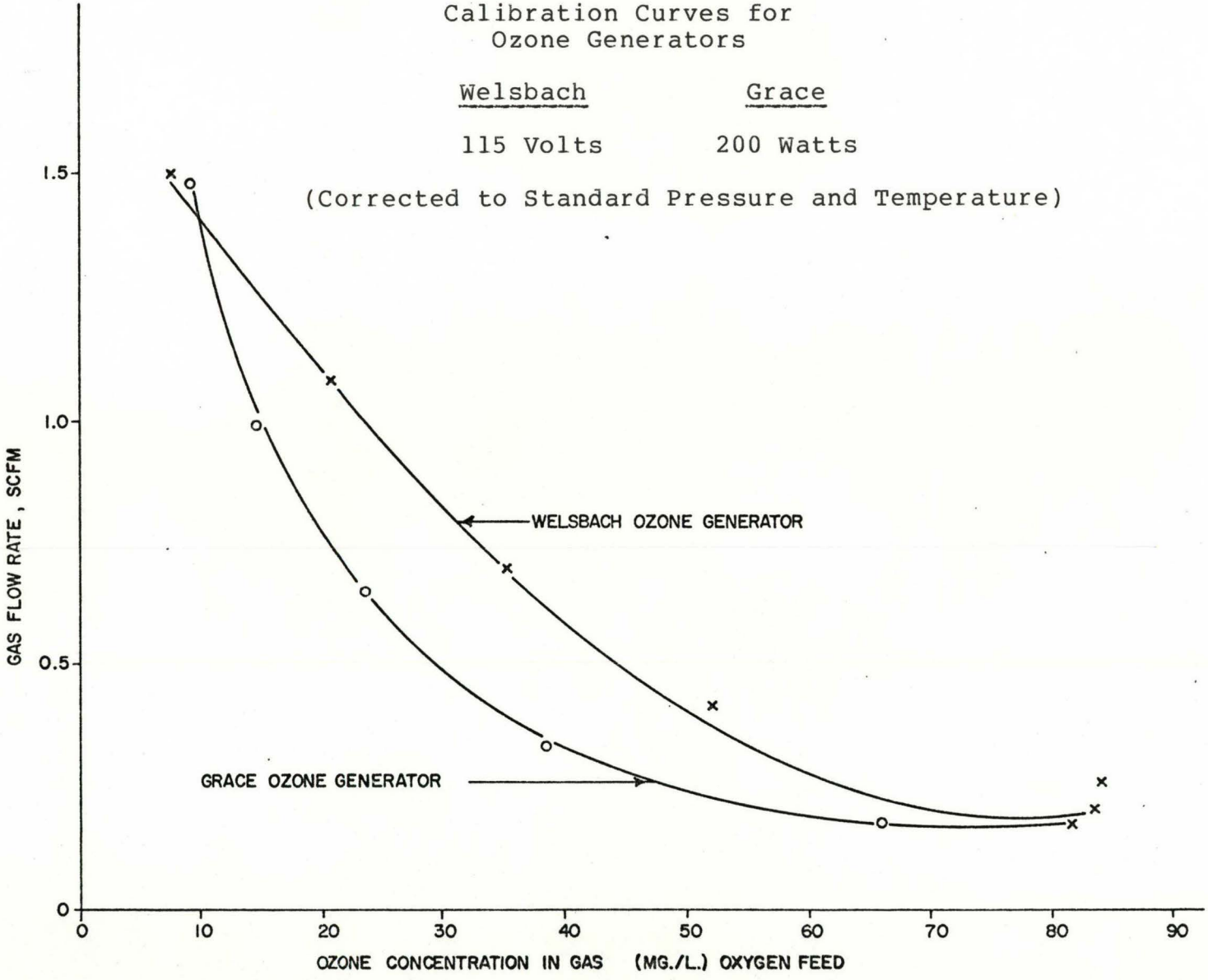


FIGURE 5

Laboratory Tests for Bacteria Survival
in Ozonated Water: Bacillus Polymyxas Spores
(Ozone Concentration not Monitored)

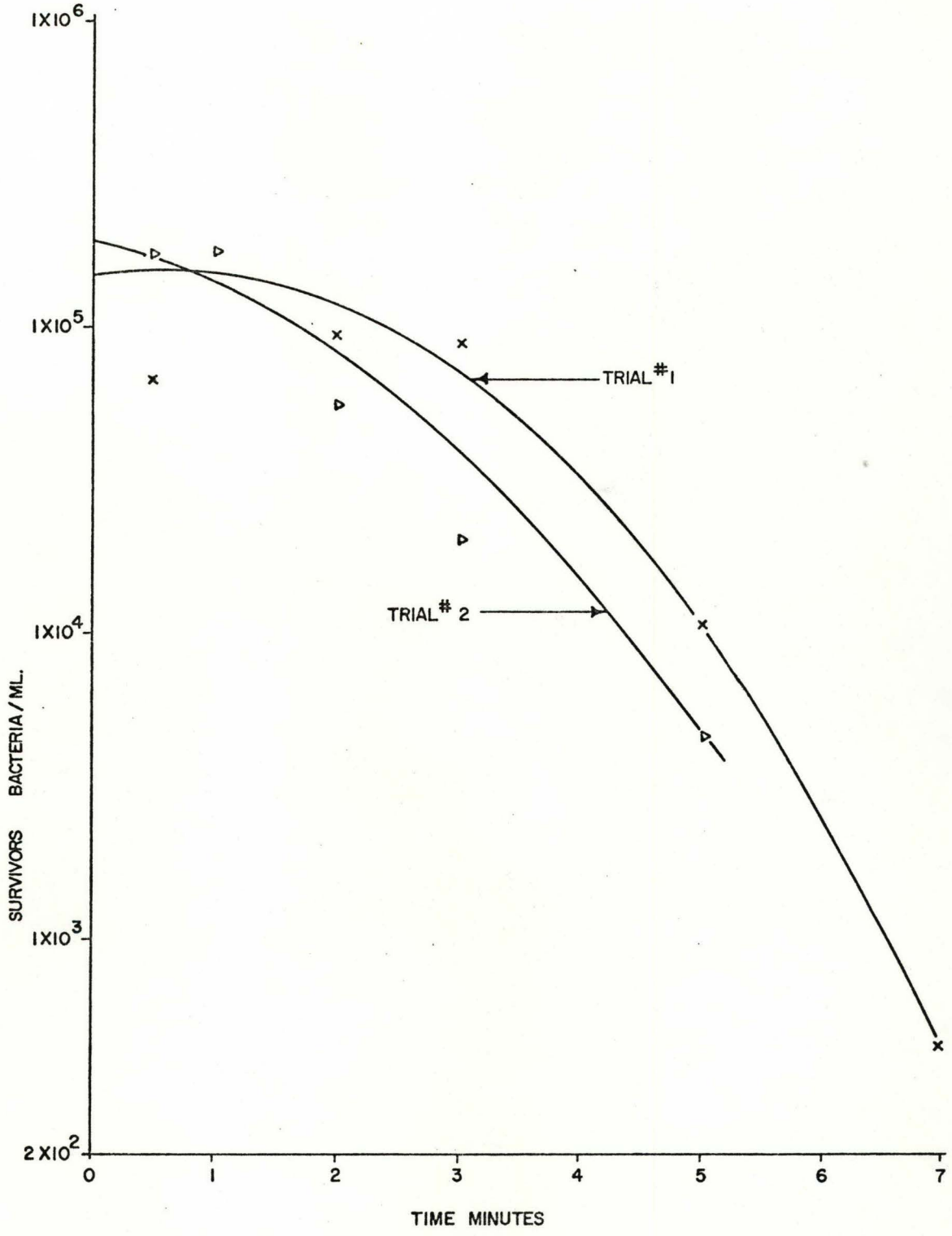


FIGURE 6

Laboratory Tests for Bacteria Survival
in Ozonated Water: Aeromonas Liquifaciens
(Ozone Concentration not Determined)

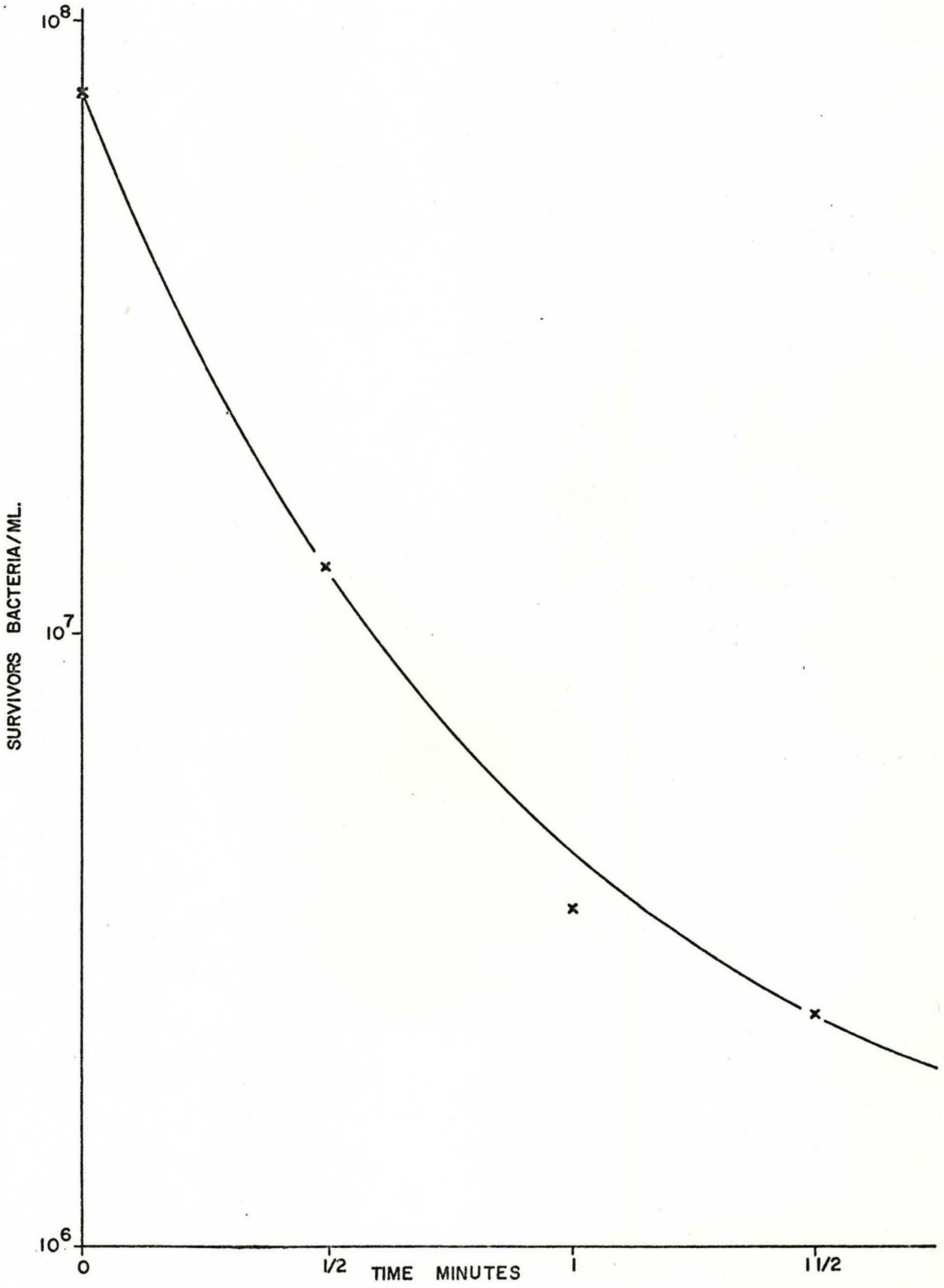
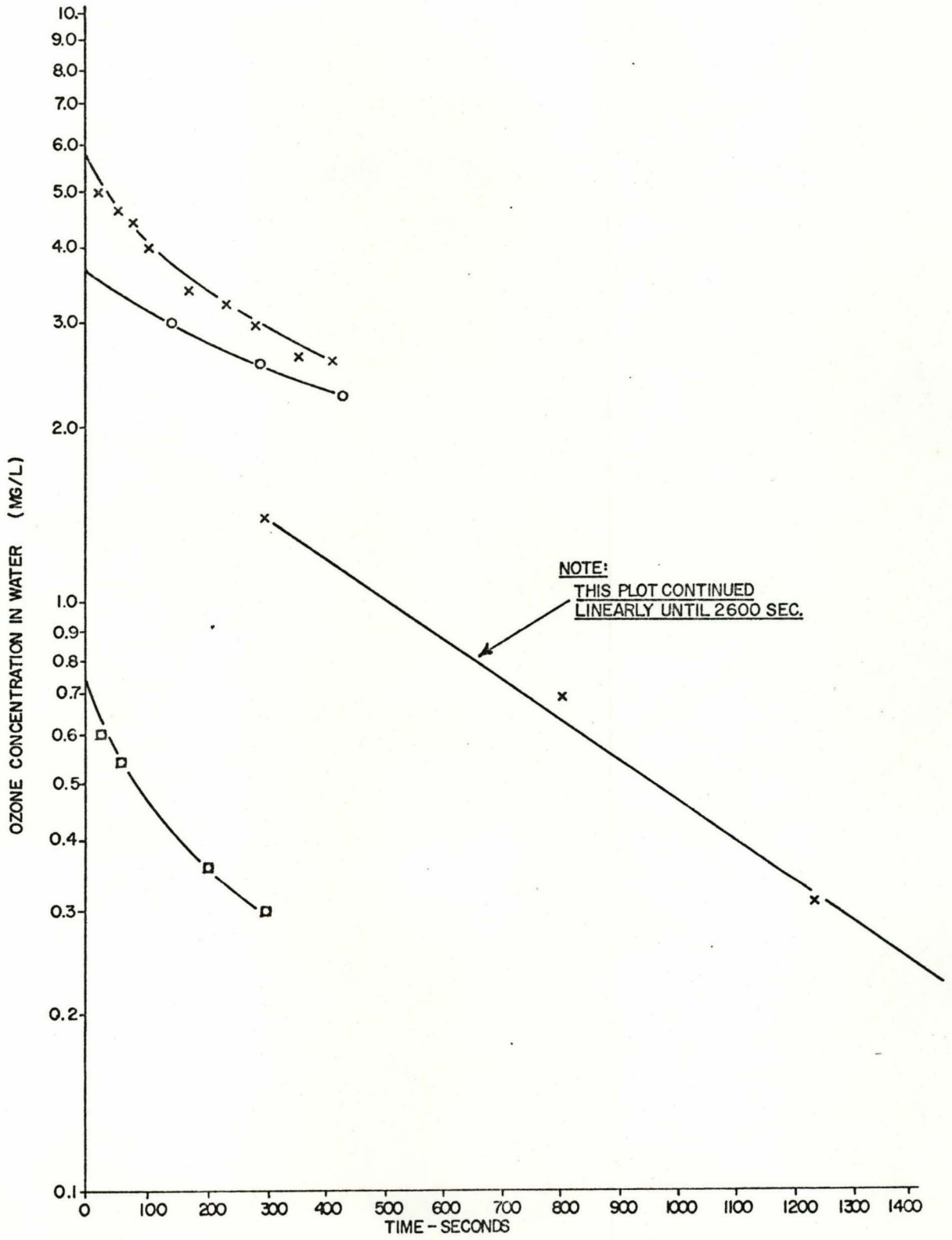
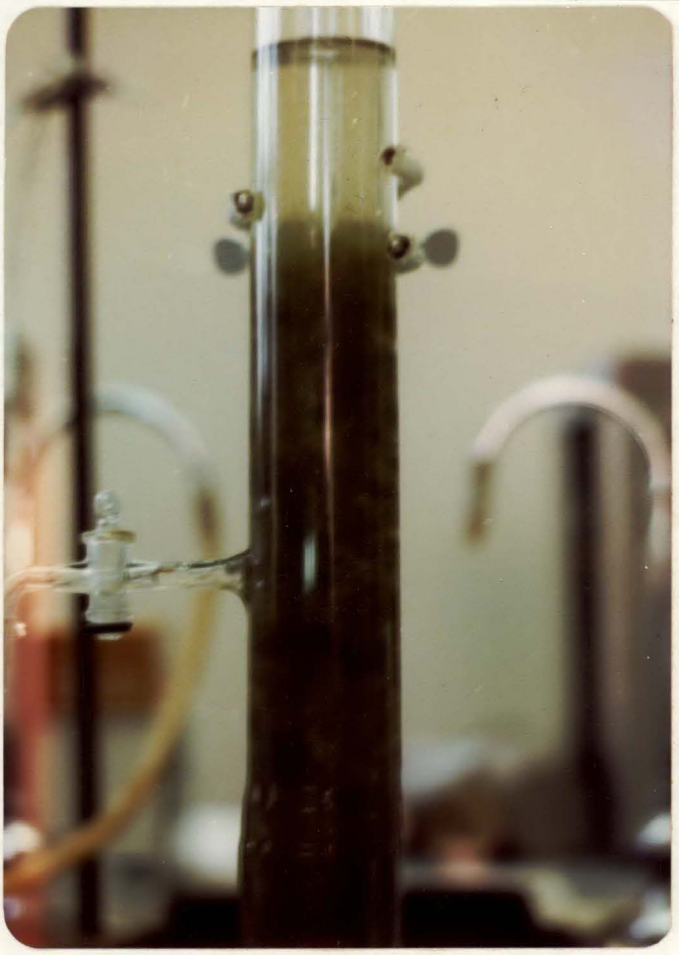


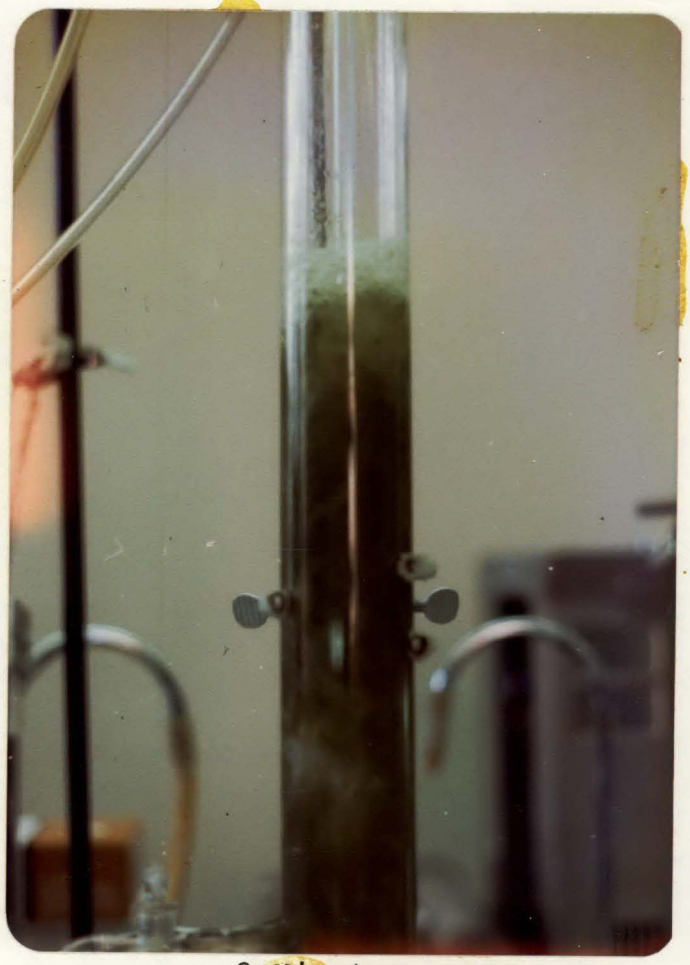
FIGURE 7

Ozone Decay in Raw River Water
at Dworshak

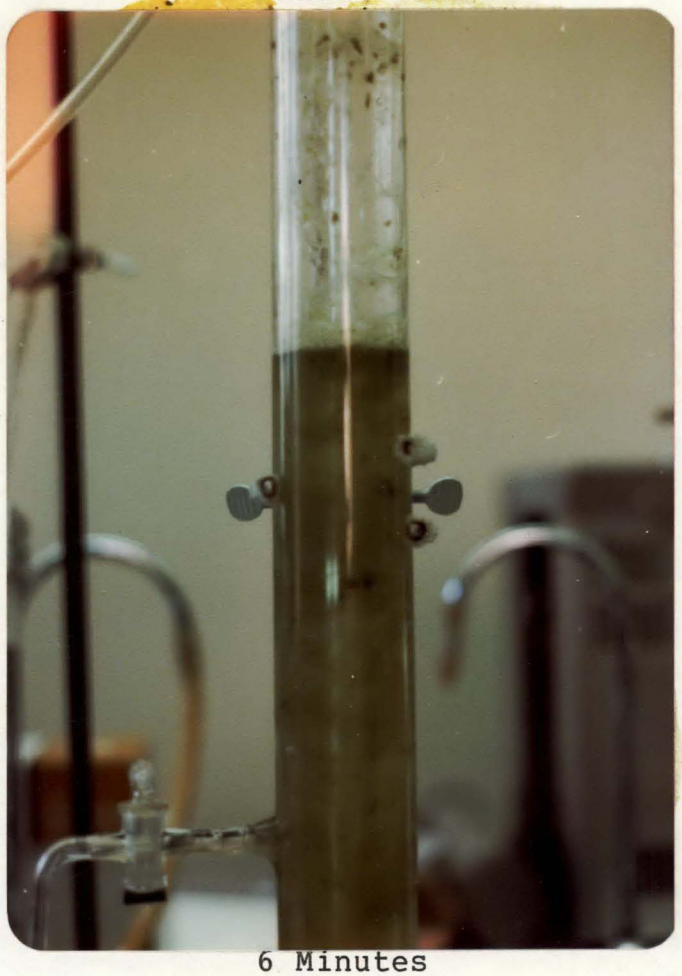




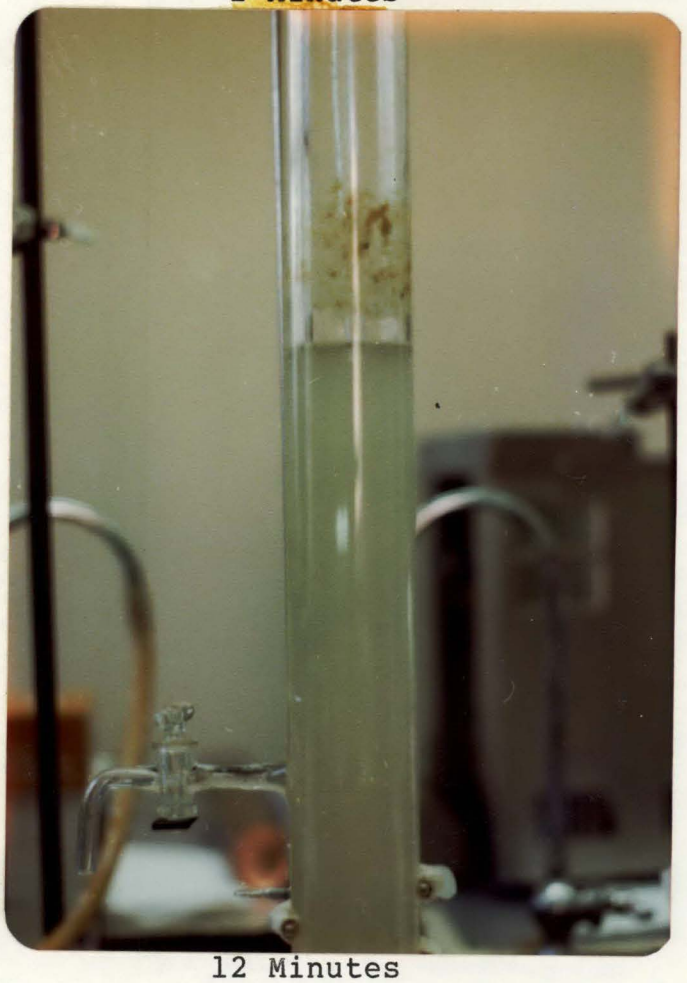
Before Ozone



2 Minutes



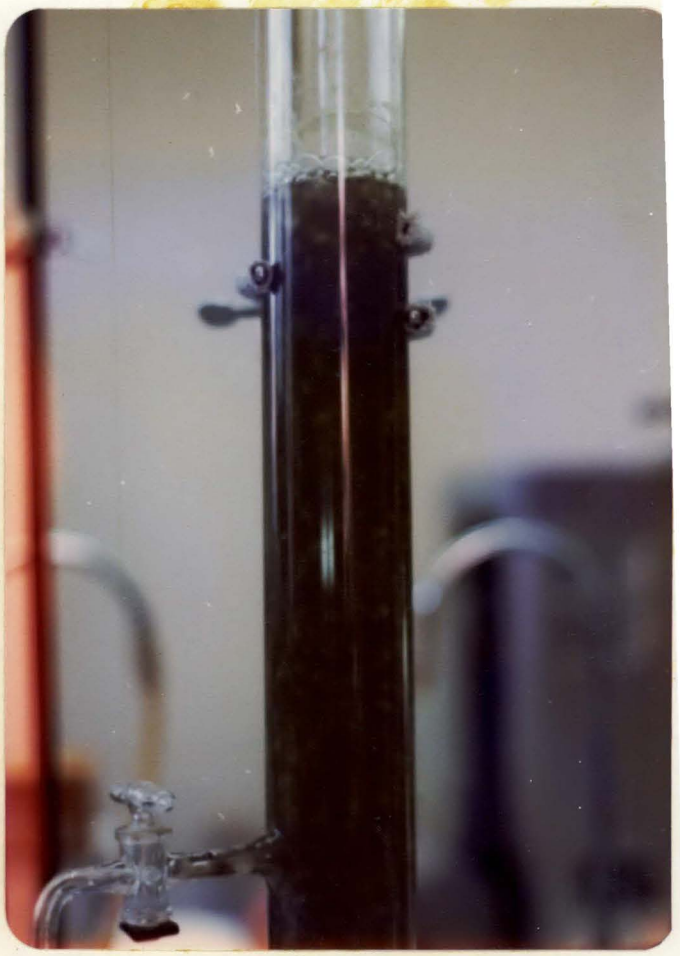
6 Minutes



12 Minutes

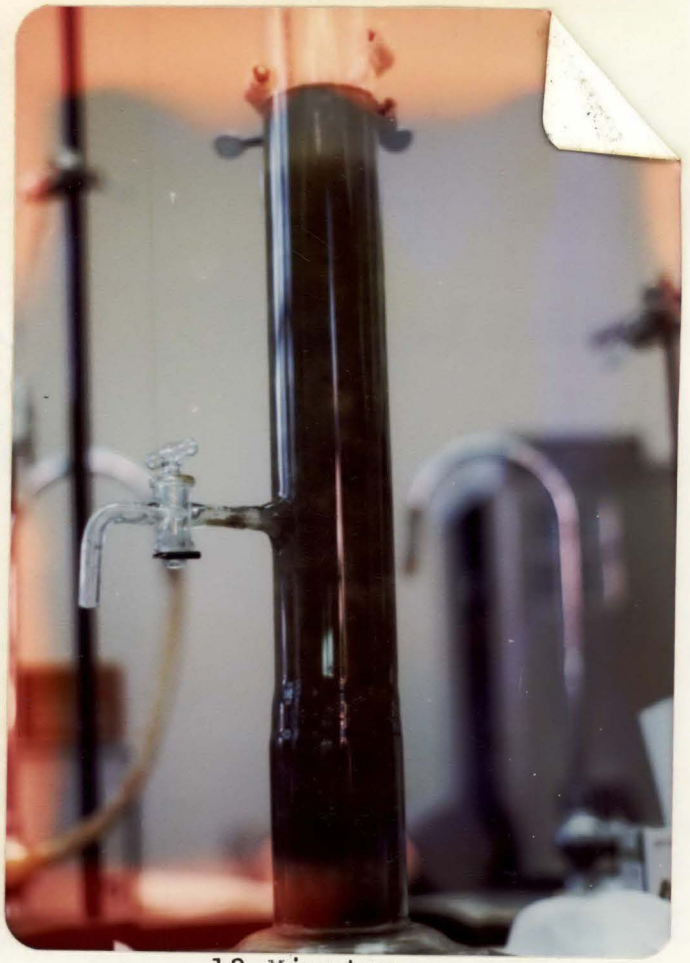
Figure 8
Ozone Affects on Algae

Before Oxygen



2 Minutes

6 Minutes



12 Minutes

Figure 9
Oxygen Affects on Algae

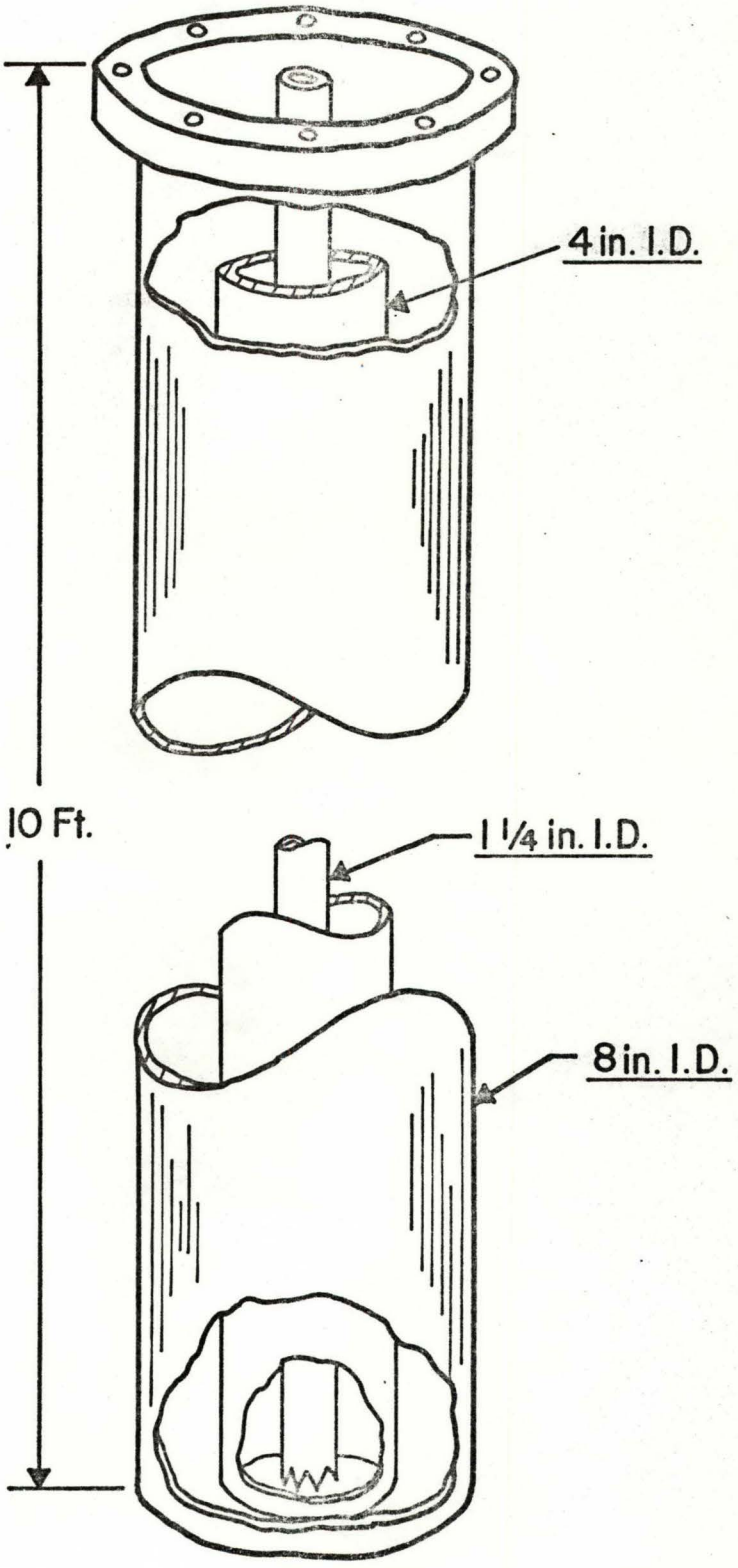


Figure 10. Ozone Contact Column

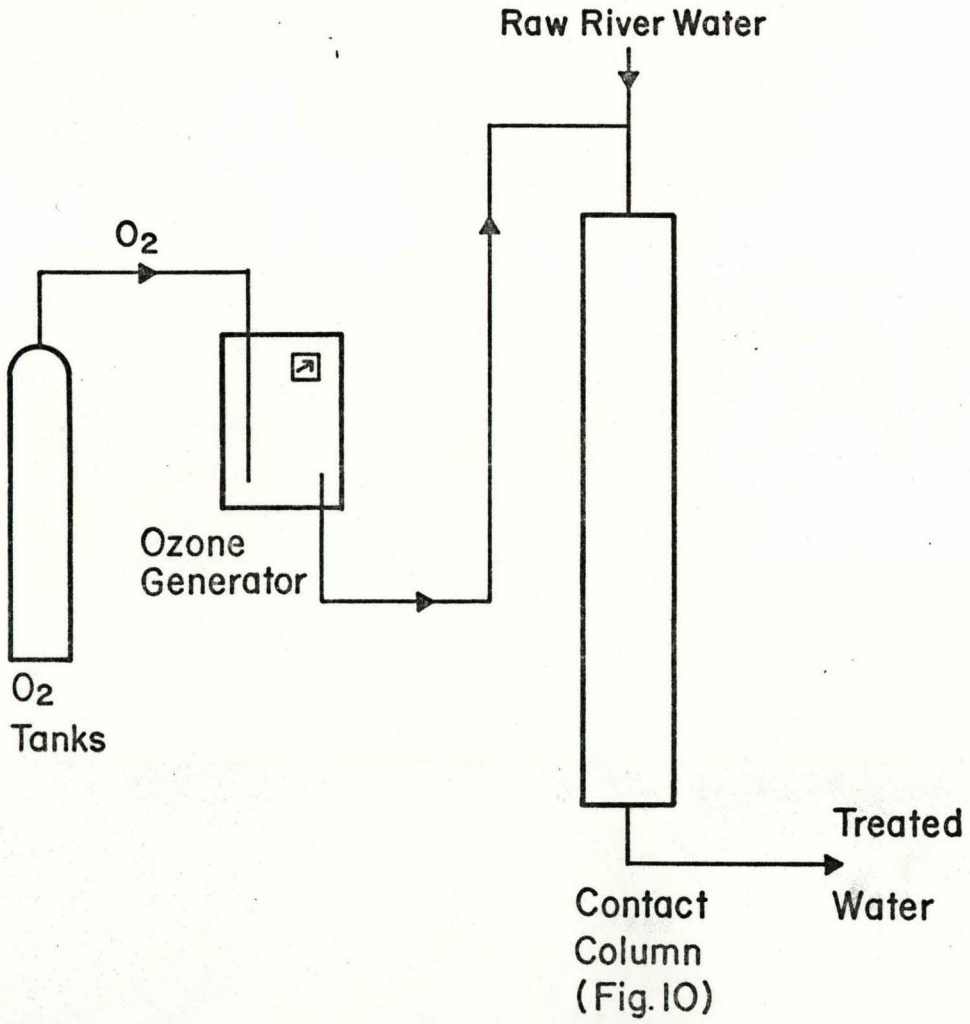


Figure 11. Flow Schematic, Ozone Pilot Plant At Dworshak National Fish Hatchery

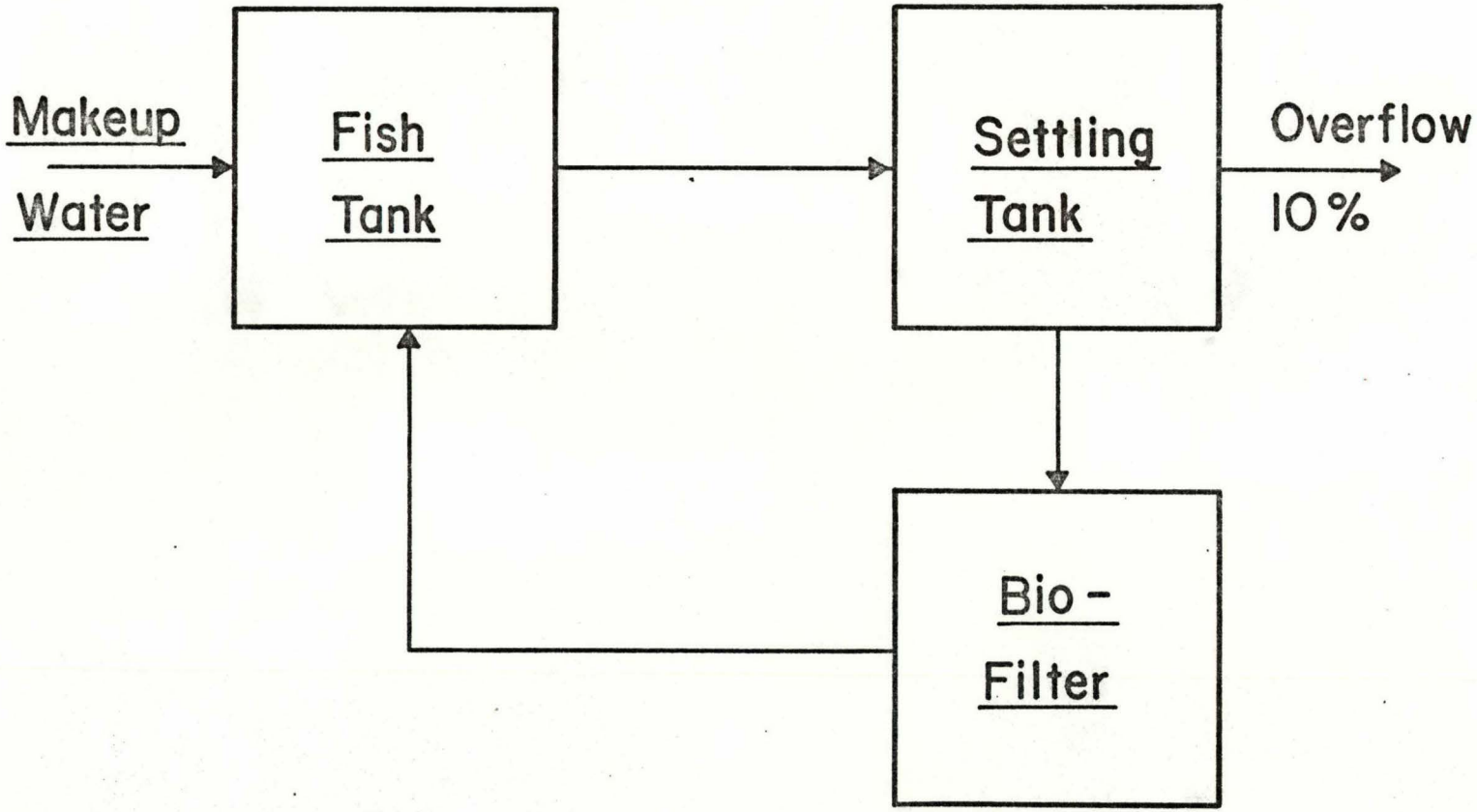


Figure 12. Flow Schematic, Existing Biofilter Pilot Plant At Dworshak

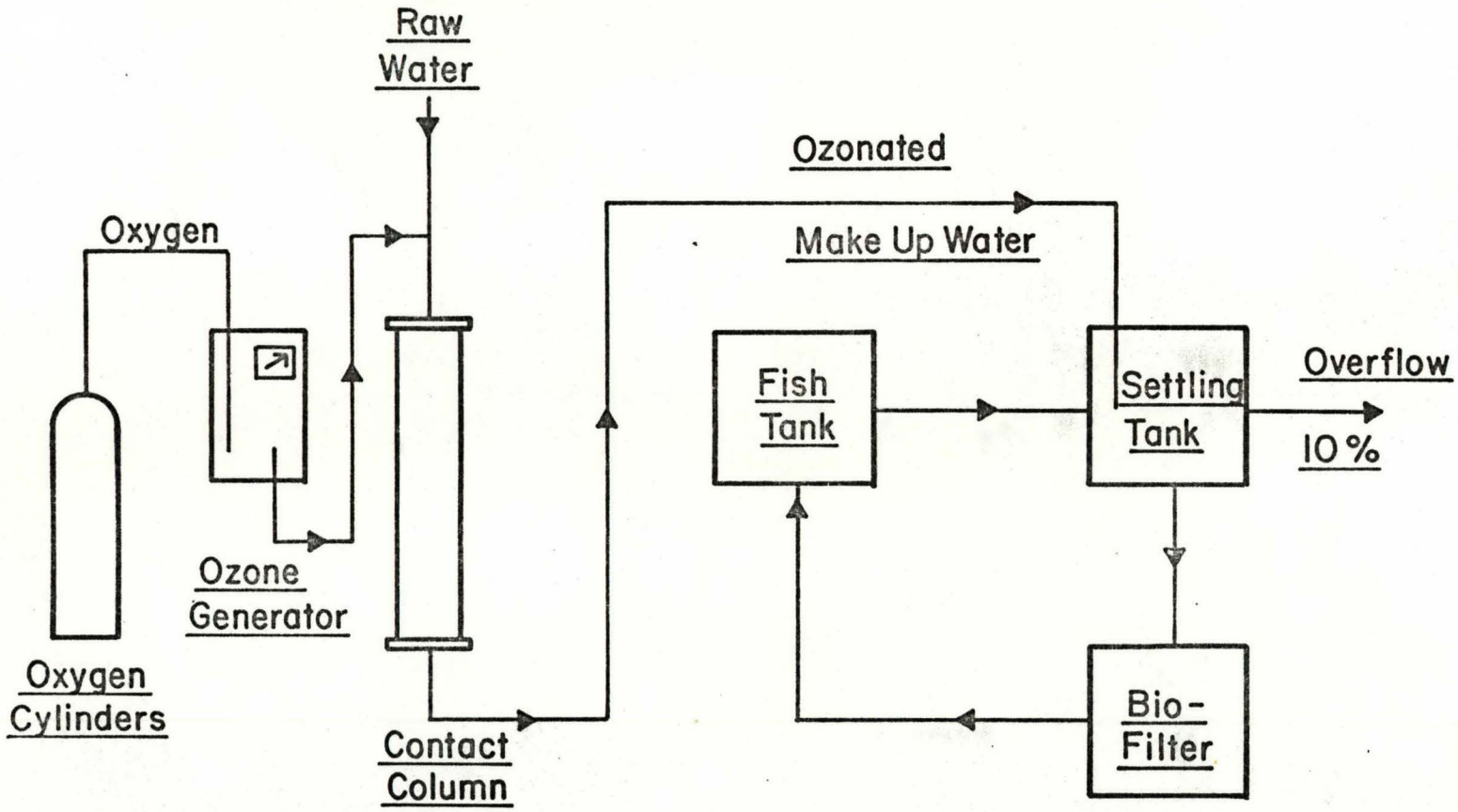


Figure 13. Flow Schematic - Integrated Pilot Plant: Make Up Water Ozone Treatment

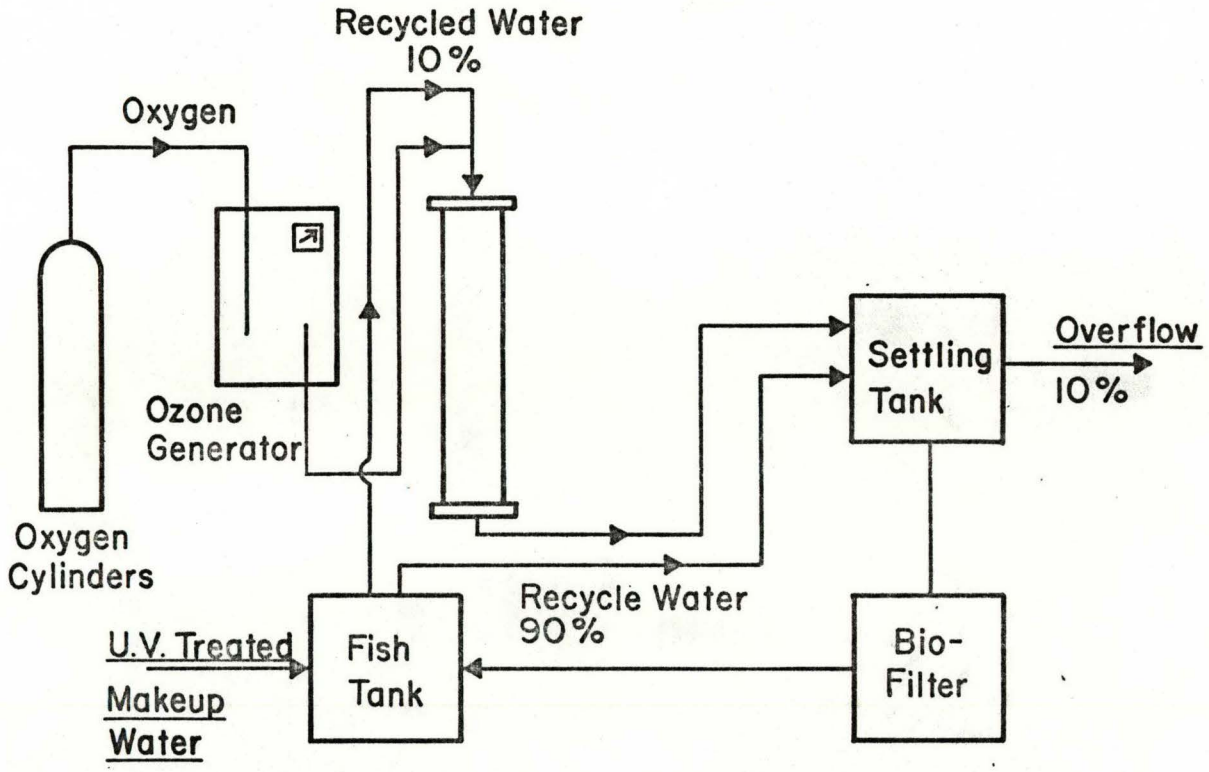
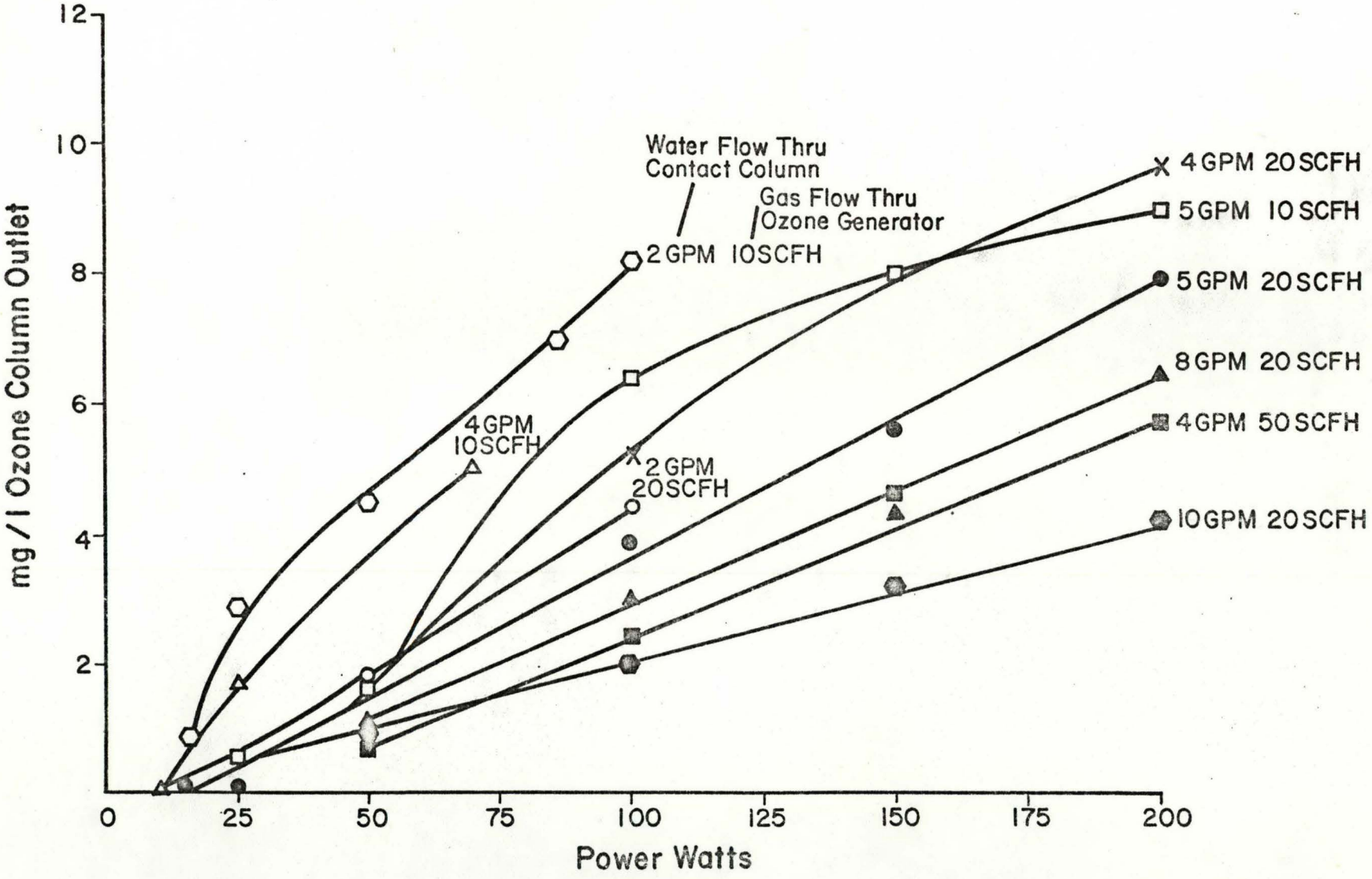


Figure 14. Flow Schematic – Integrated Pilot Plant: Recycle Water Ozone Treatment

FIGURE 15

Residual Ozone (Mg/l) in Water
Measured at Ozone Pilot Plant Column Outlet
Grace Ozone Generator
River Water Feed
Oxygen Feed Gas



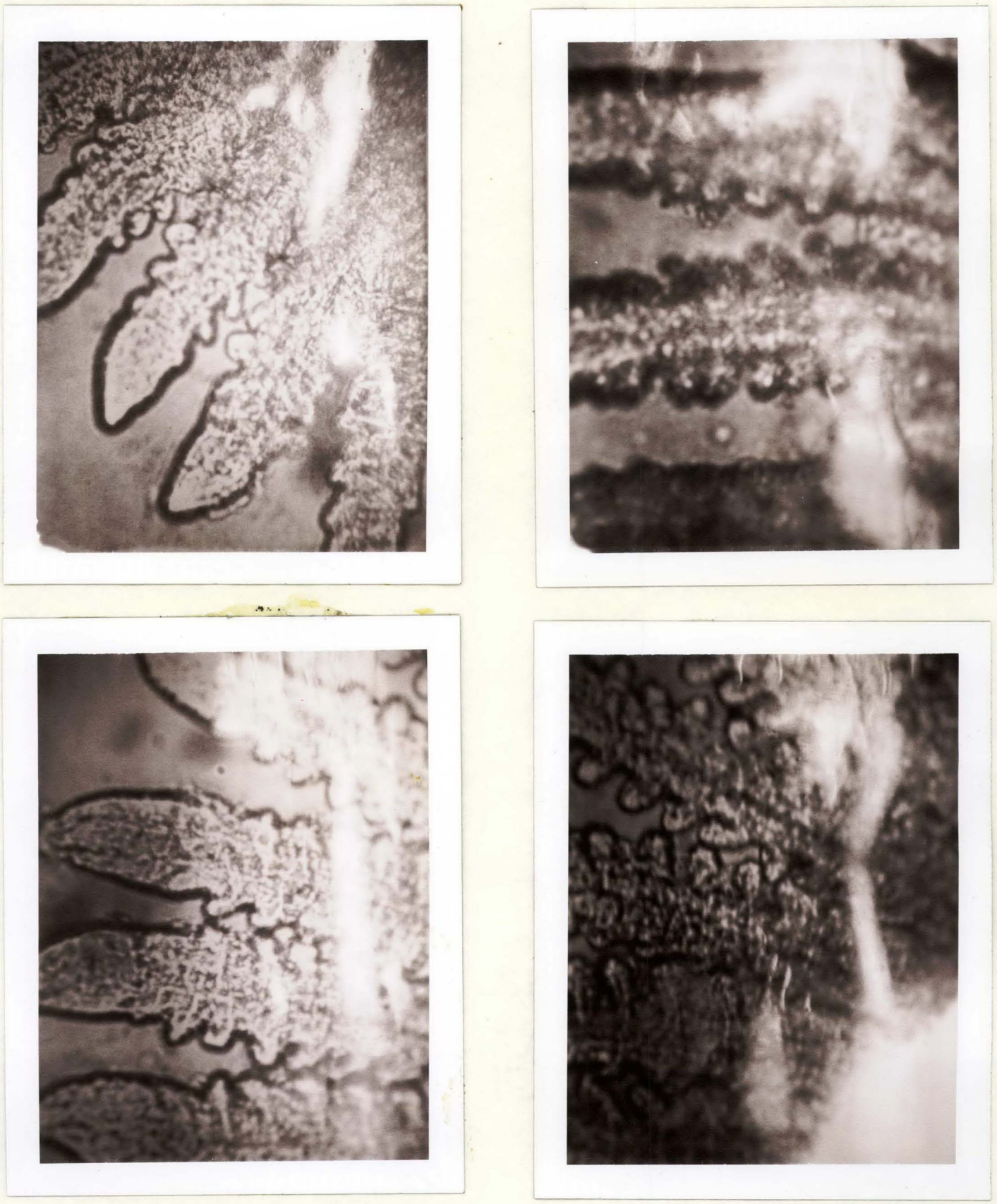


Figure 16
Microscope View - Steelhead Fry
Control Fish - First Gill Arch
Prior to Placement in Pilot Plant

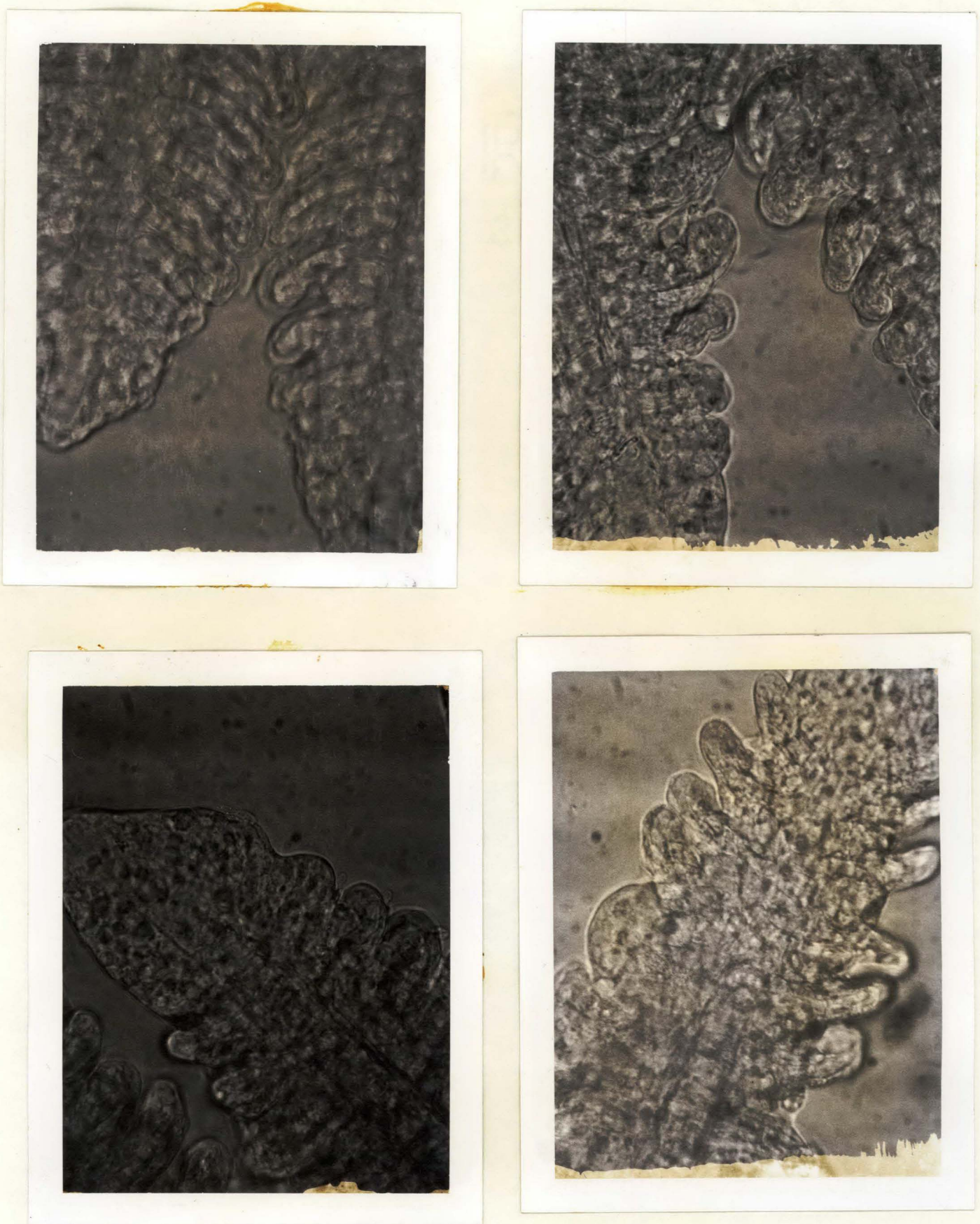


Figure 17
Microscope View - Steelhead Fry
Post Ozone Run - Pre-Mortality Study
Fish Gill Arch

FIGURE 18

UV System Outlet
Total Bacteria Count

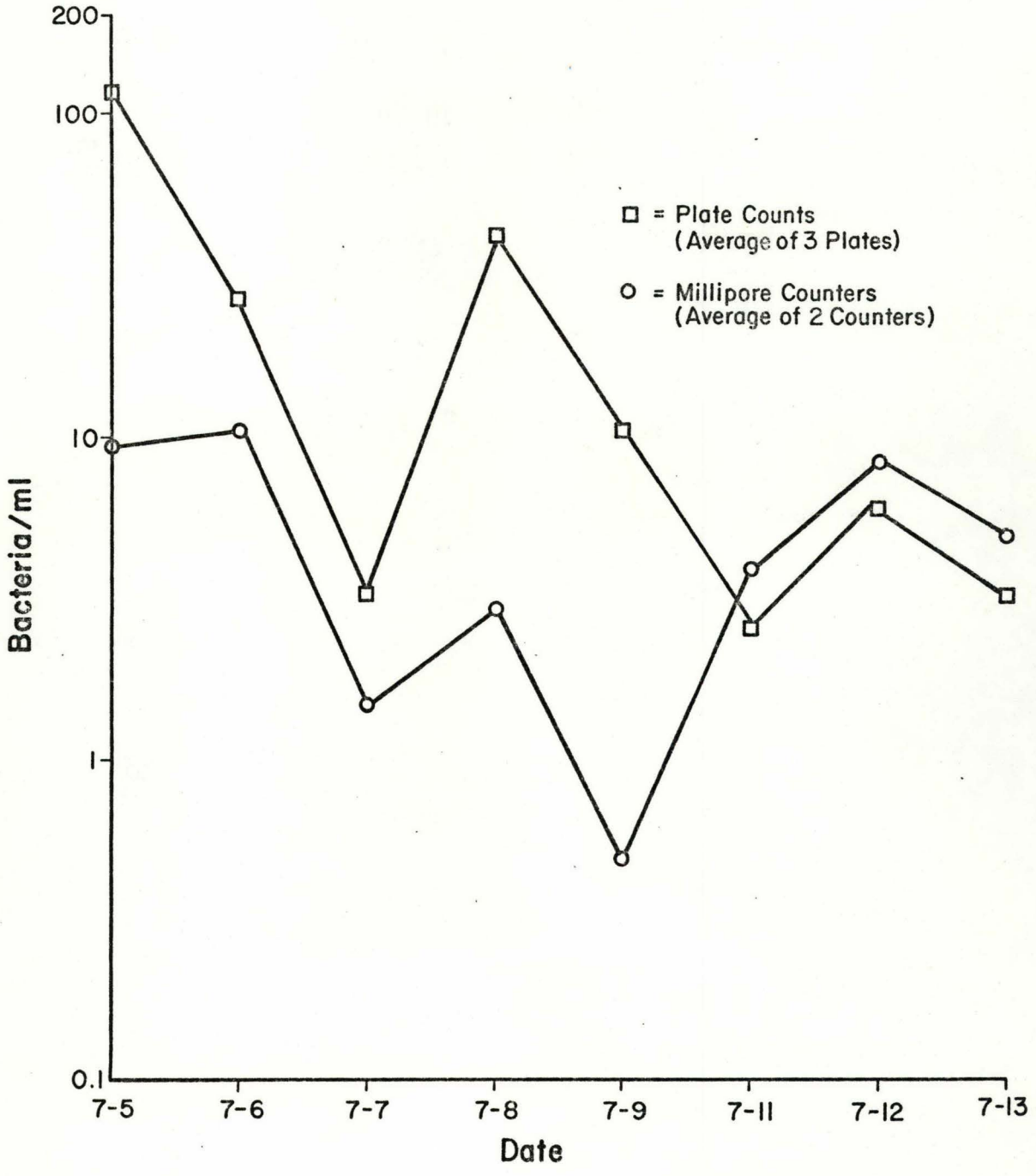
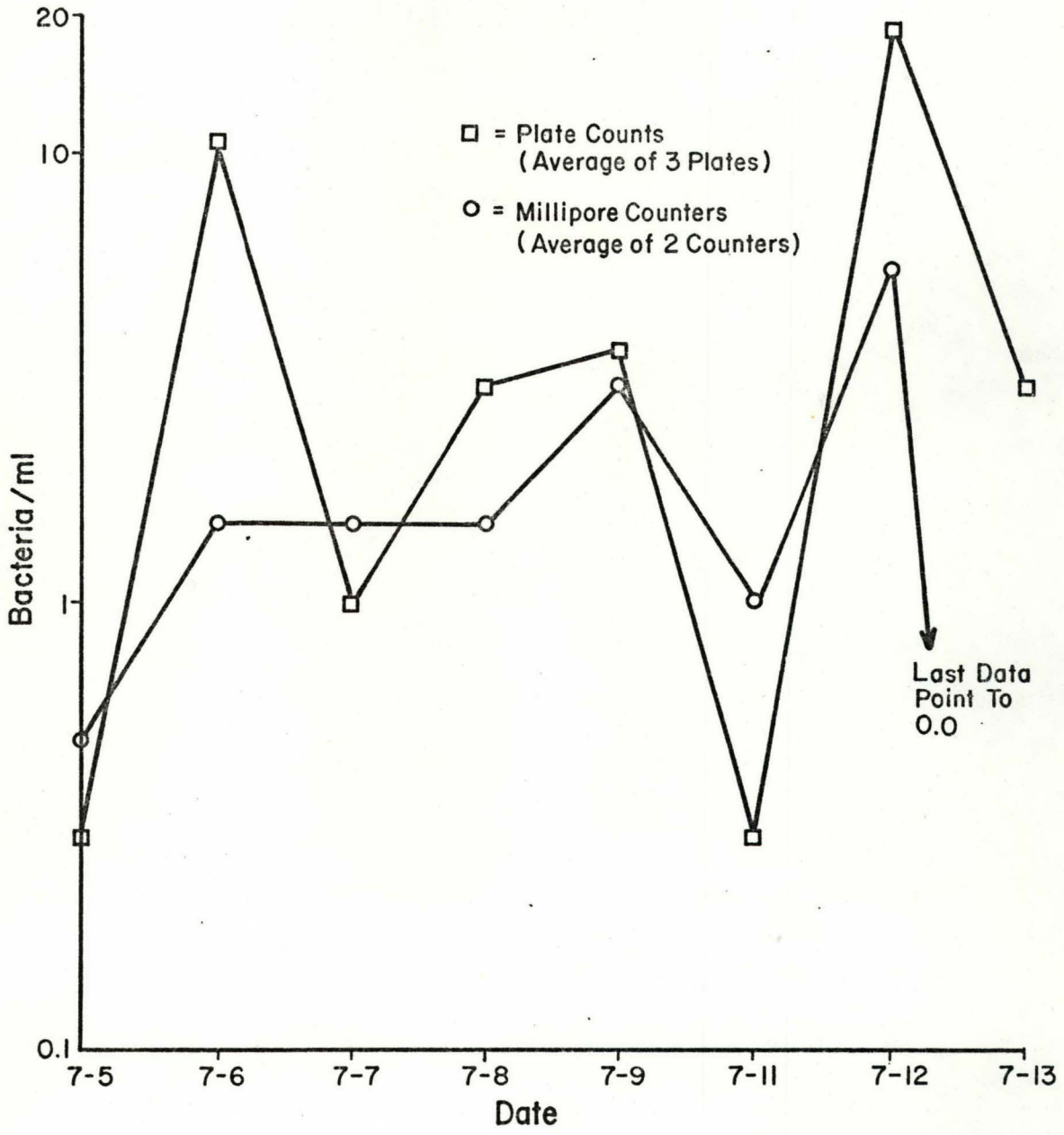


FIGURE 19

Total Bacteria Count
Ozone Column Outlet During
Continuous Ozonation Run



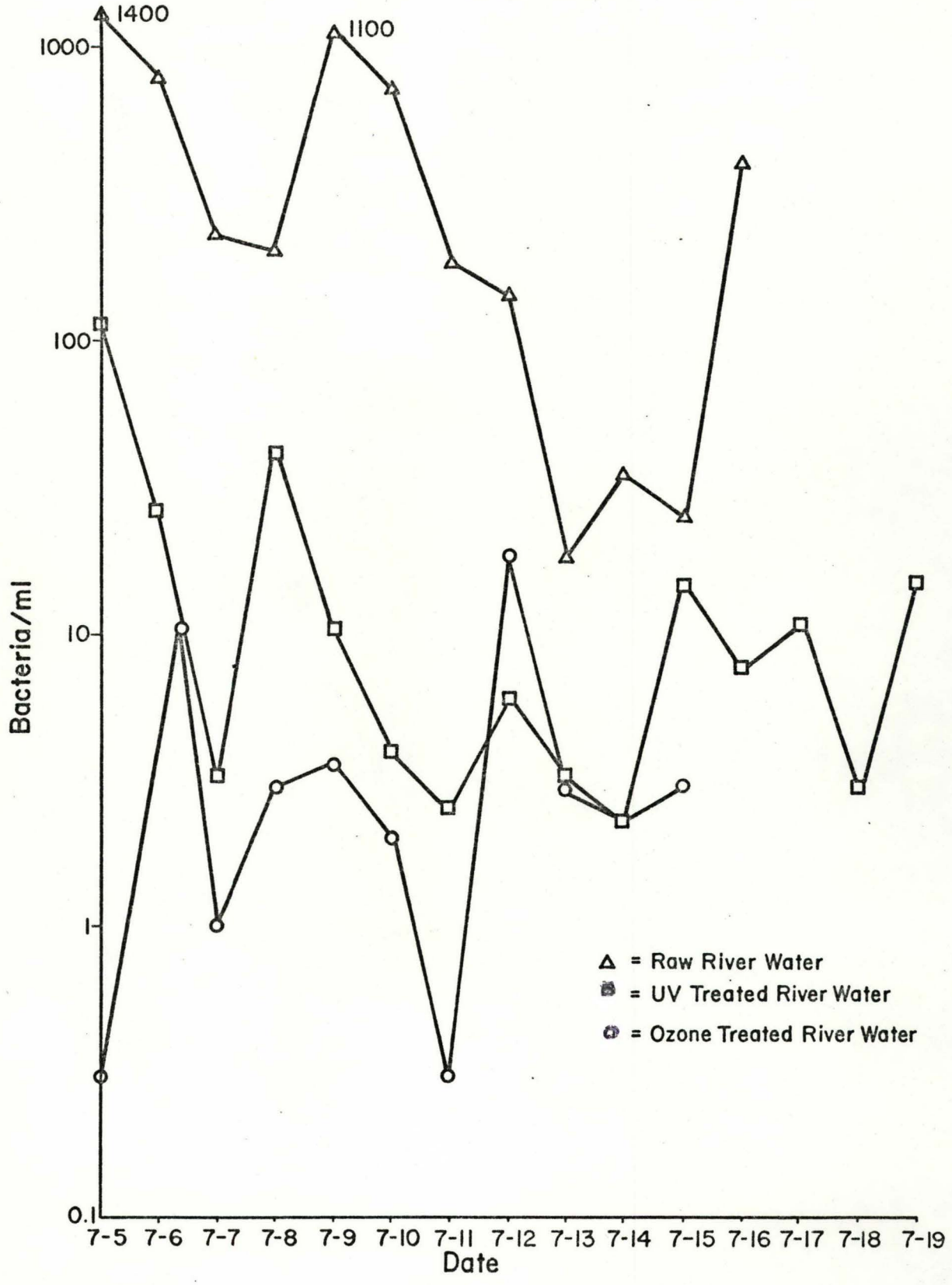
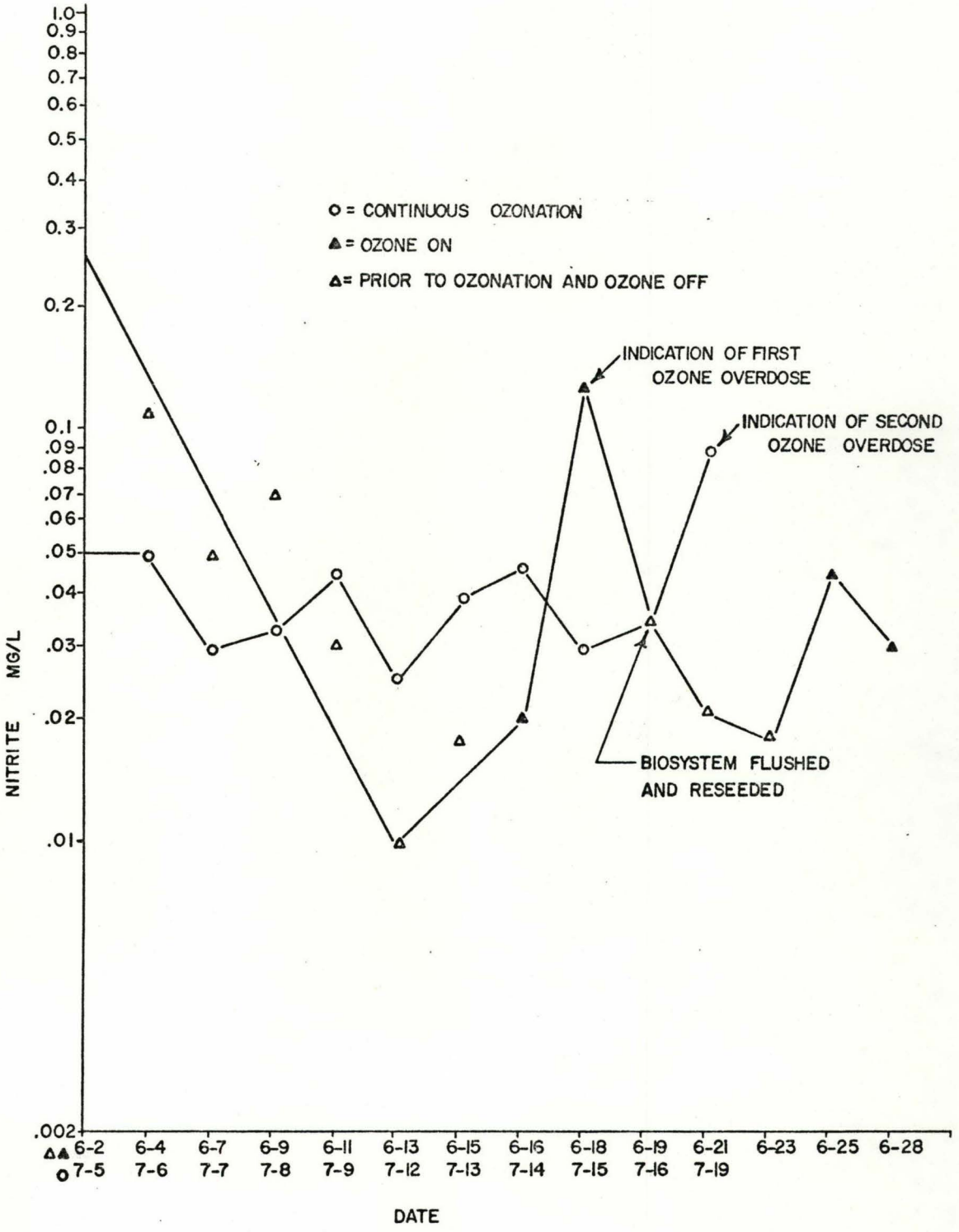


FIGURE 20

Total Bacteria During Continuous Ozonation Run
Plate Counts - Average of Three Plates Per Sample

FIGURE 21

Biofilter Pilot Plant Nitrite Concentrations Before and During Continuous Ozonation Trial Run (Values from Fish Tank)



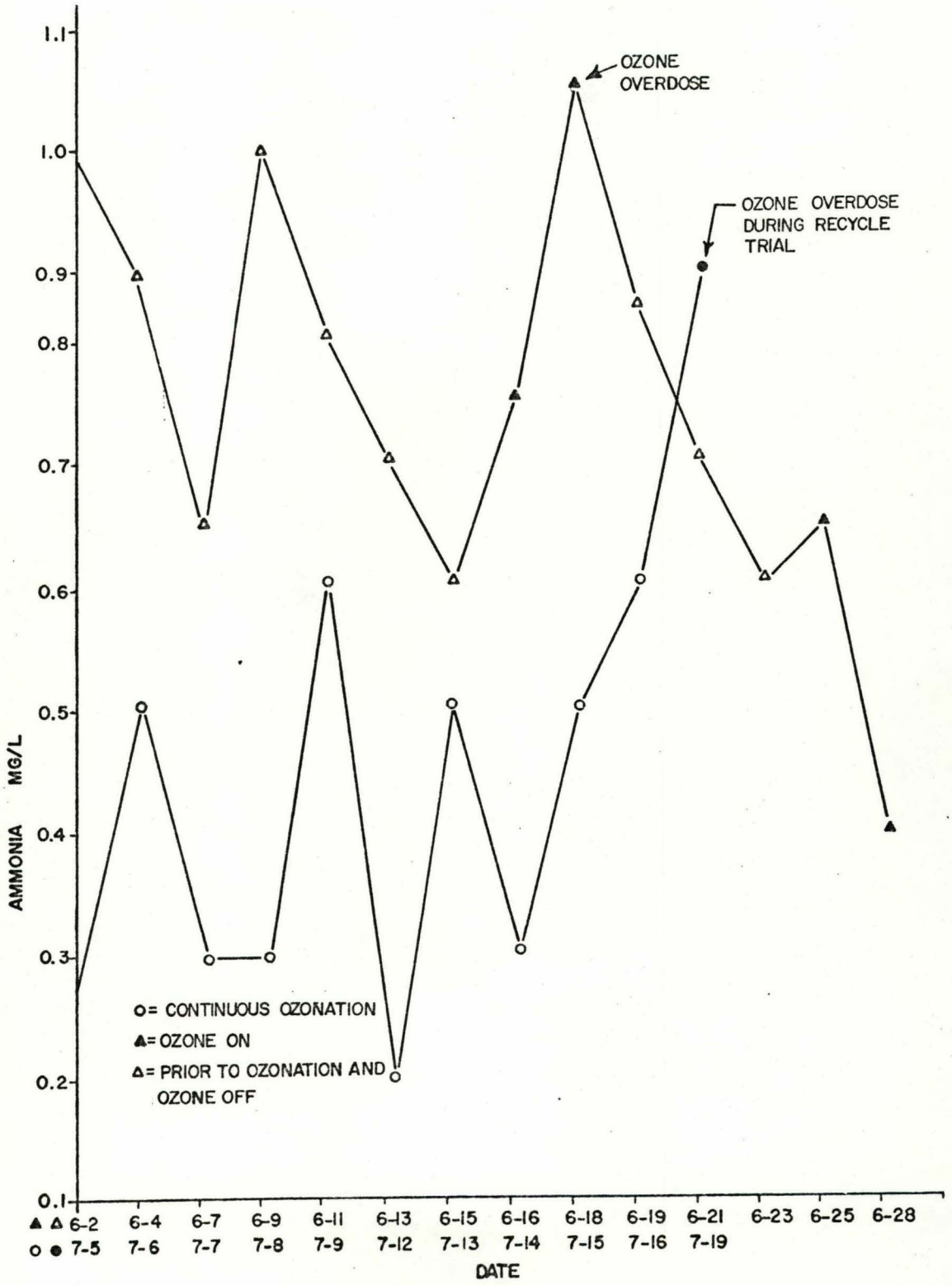


FIGURE 22

Biofilter Pilot Plant Ammonia Concentrations Before and During Ozonation Trial Run (Values from Fish Tank)

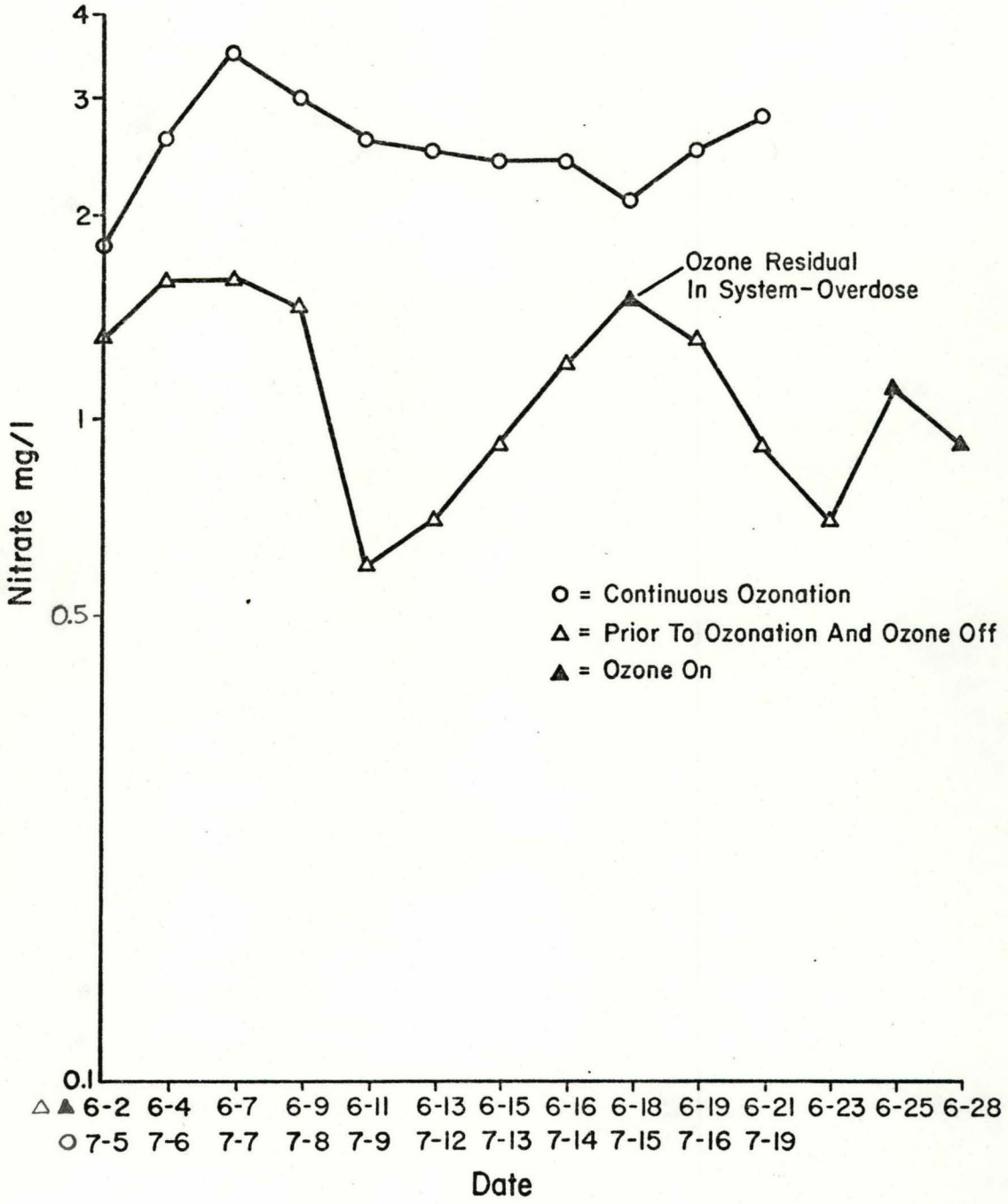


FIGURE 23

Biofilter Pilot Plant Nitrate Concentrations
Before and During Ozonation Trial Run
(Values from Fish Tank)

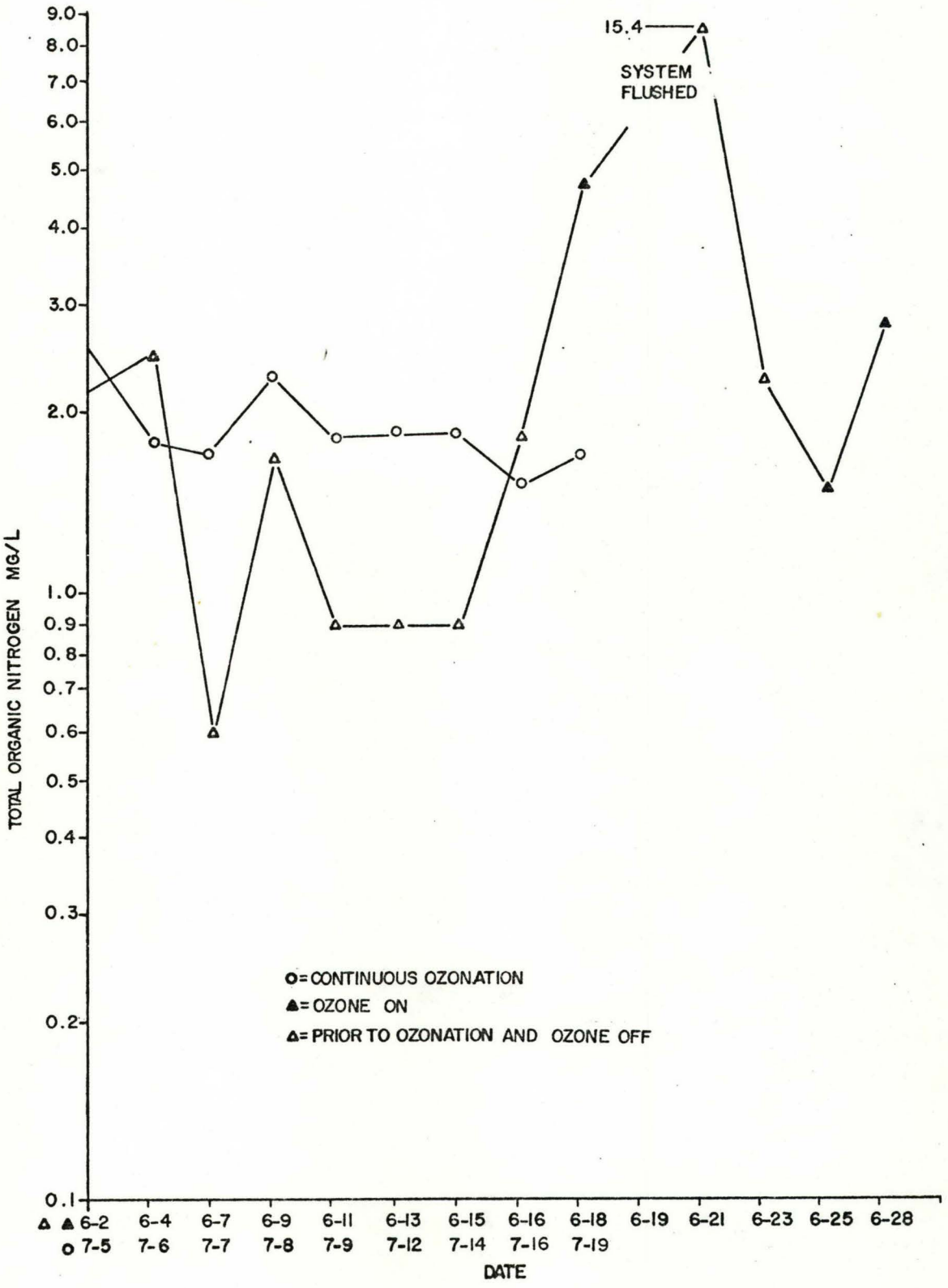


FIGURE 24

Biofilter Pilot Plant Total Organic Nitrogen Concentration Before and During Ozonation Trial Run (Values from Fish Tank)

FIGURE 25

Biofilter Pilot Plant Biochemical Oxygen Demand Before and During Ozonation (Values from Fish Tank)

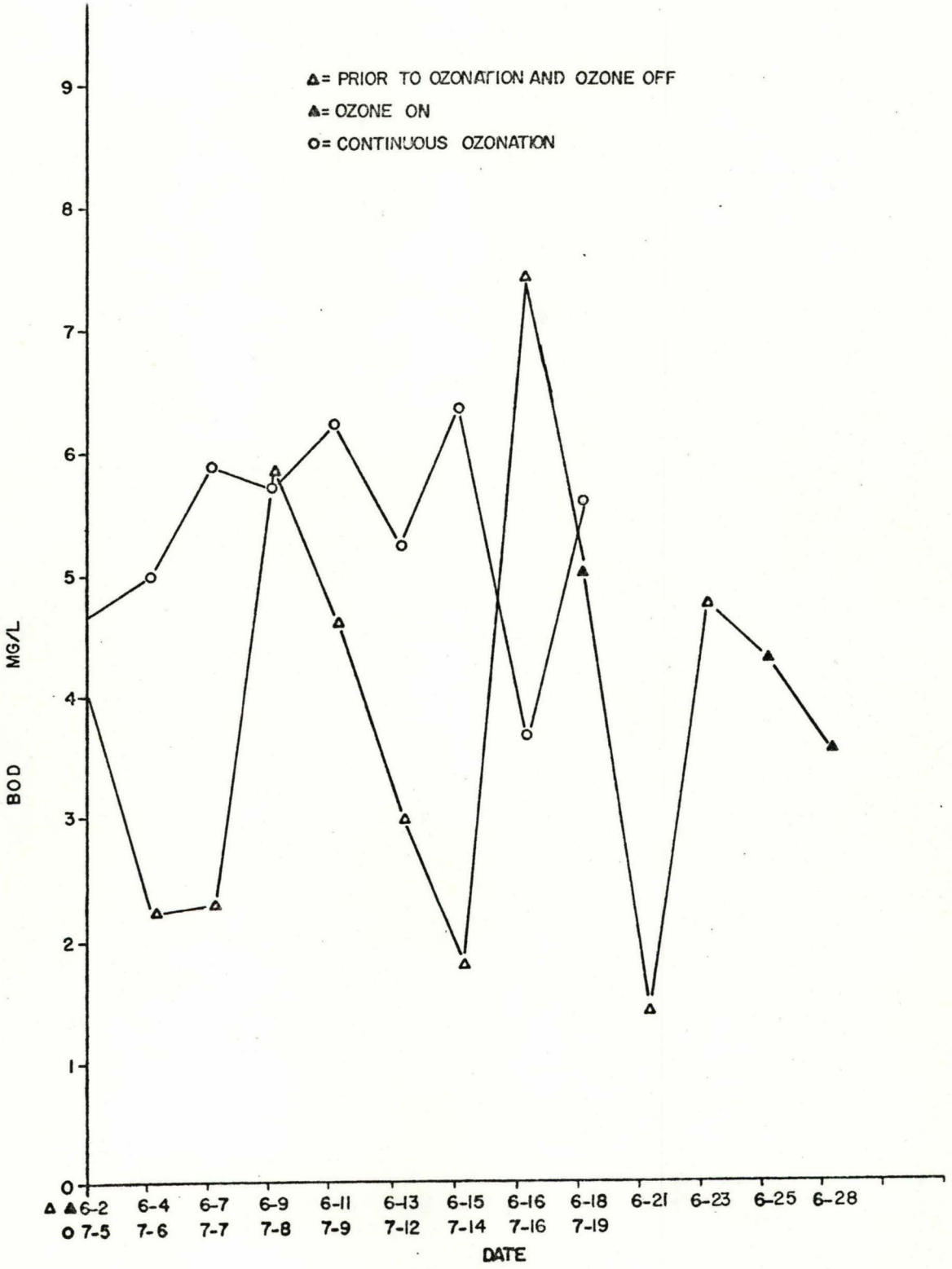


FIGURE 26

Biofilter Pilot Plant Alkalinity
Before and During Ozonation Trial Run
(Values from Fish Tank)

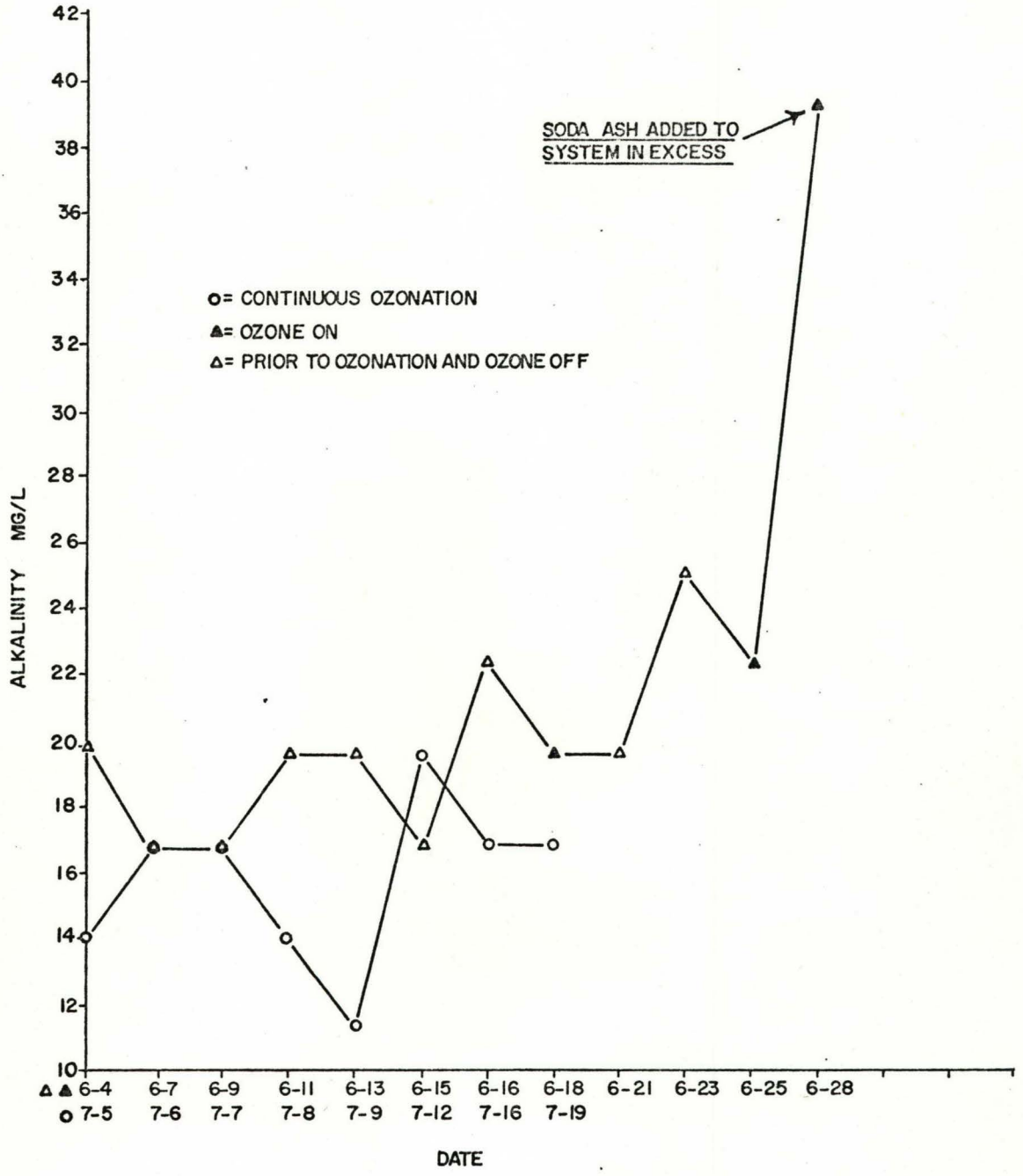
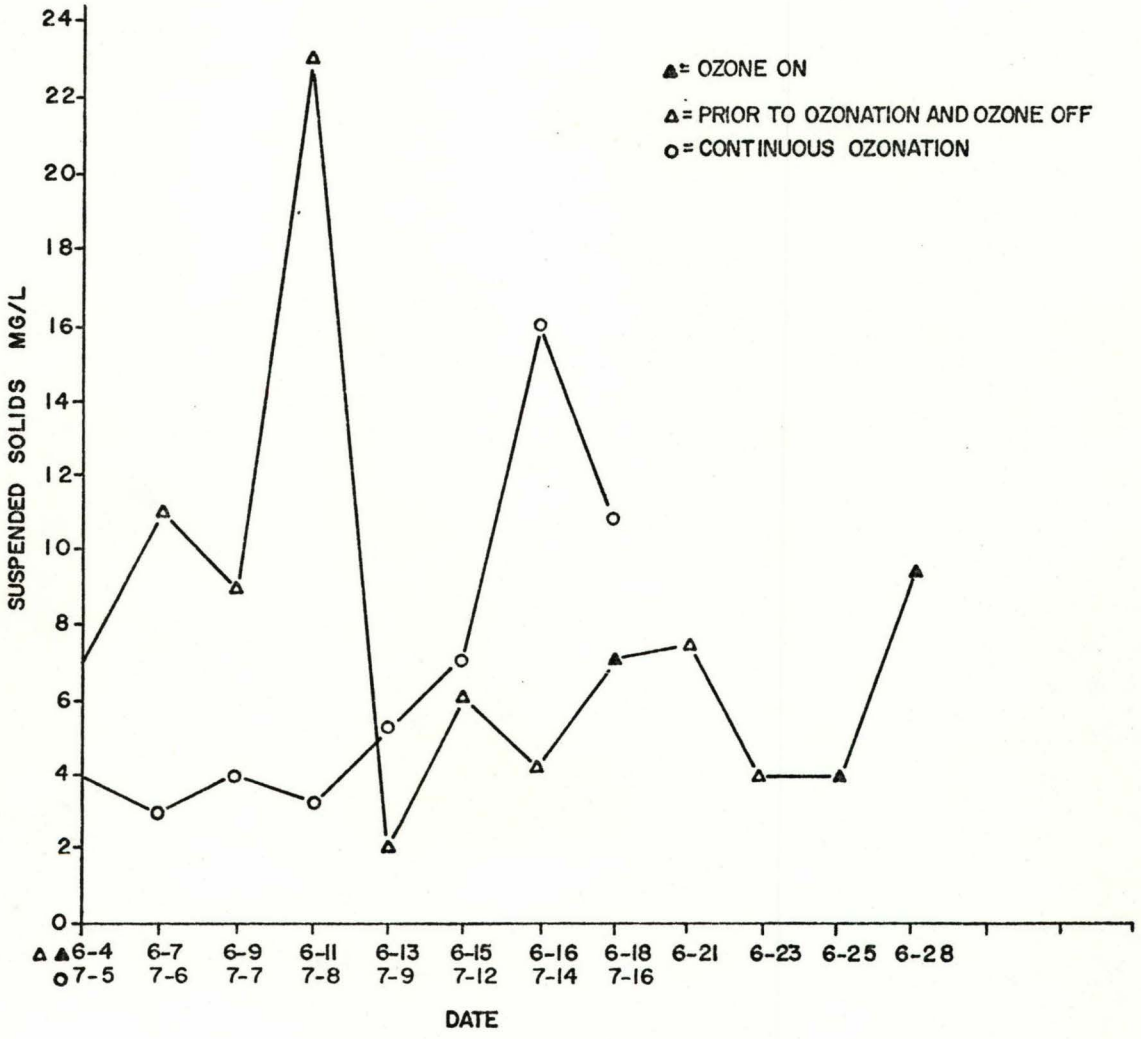


FIGURE 27

Biofilter Pilot Plant Suspended Solids
Before and During Ozonation Trial Run
(Values from Fish Tank)



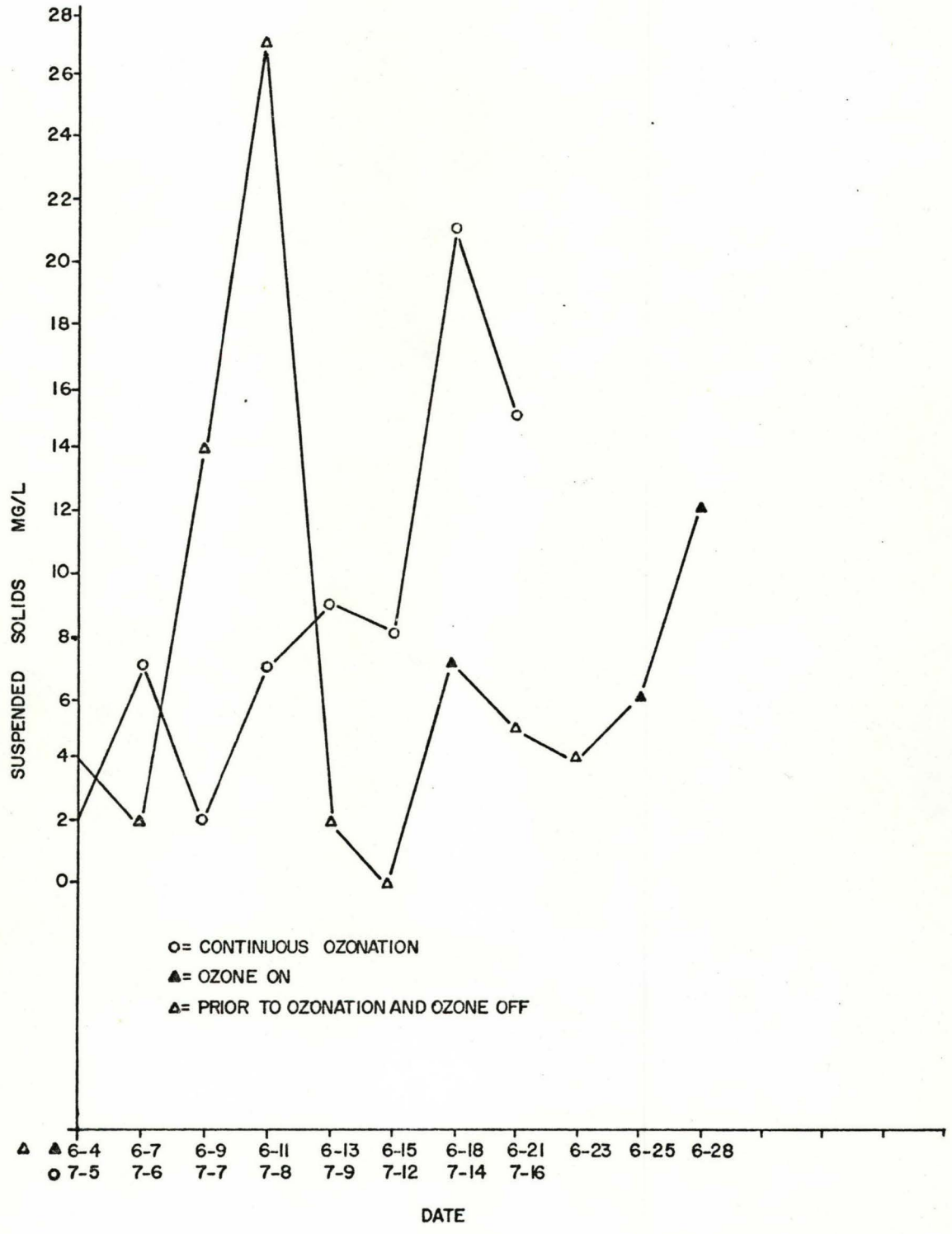


FIGURE 28

Biofilter Pilot Plant Suspended Solids
Before and During Ozonation Trial Run
(Values from Settling Tank Outlet)

FIGURE 29

Biofilter Pilot Plant Biochemical Oxygen Demand Before and During Continuous Ozonation Trial Run

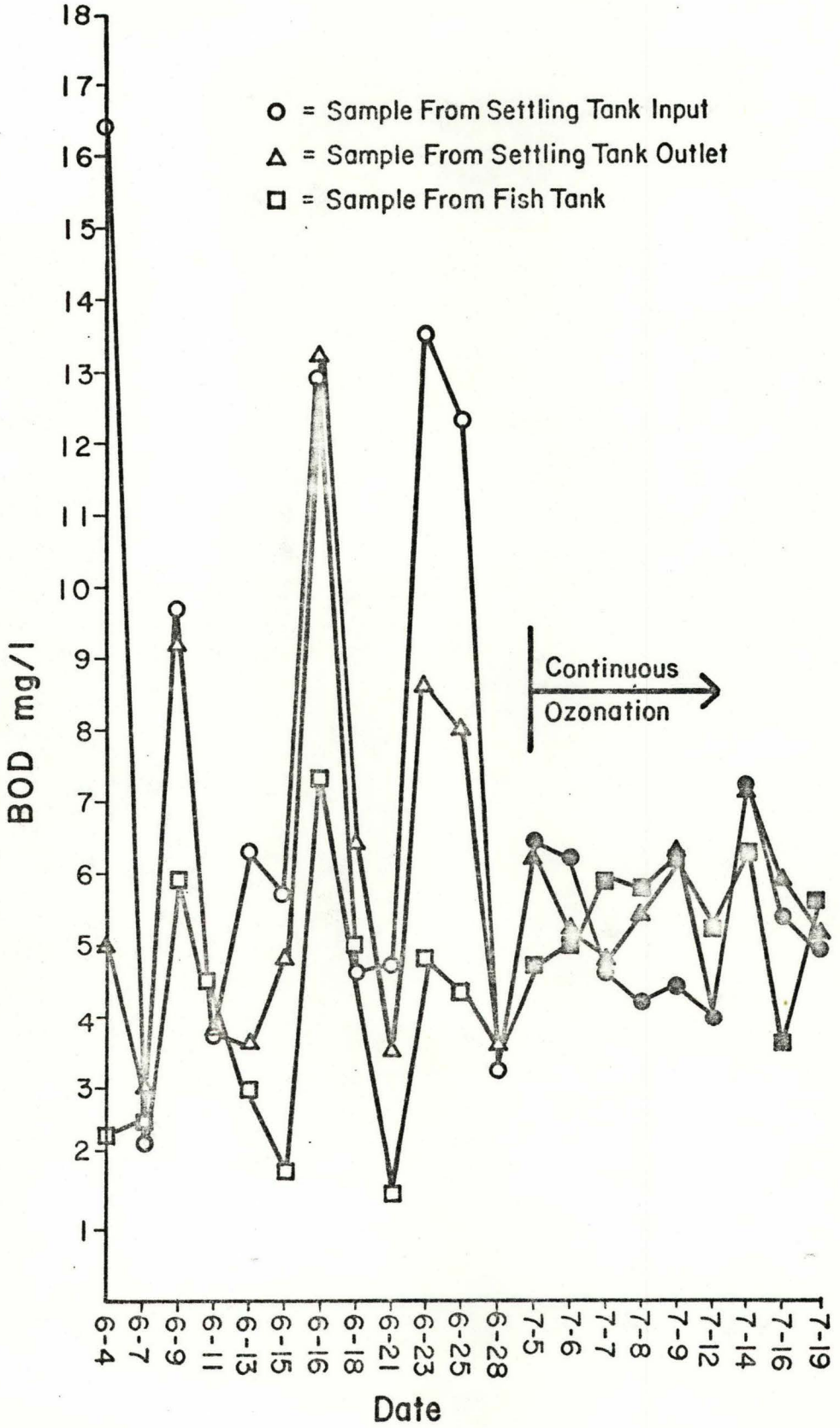


FIGURE 30

Dissolved Nitrogen
During Air Feed Gas Continuous
Ozone Sterilization Run

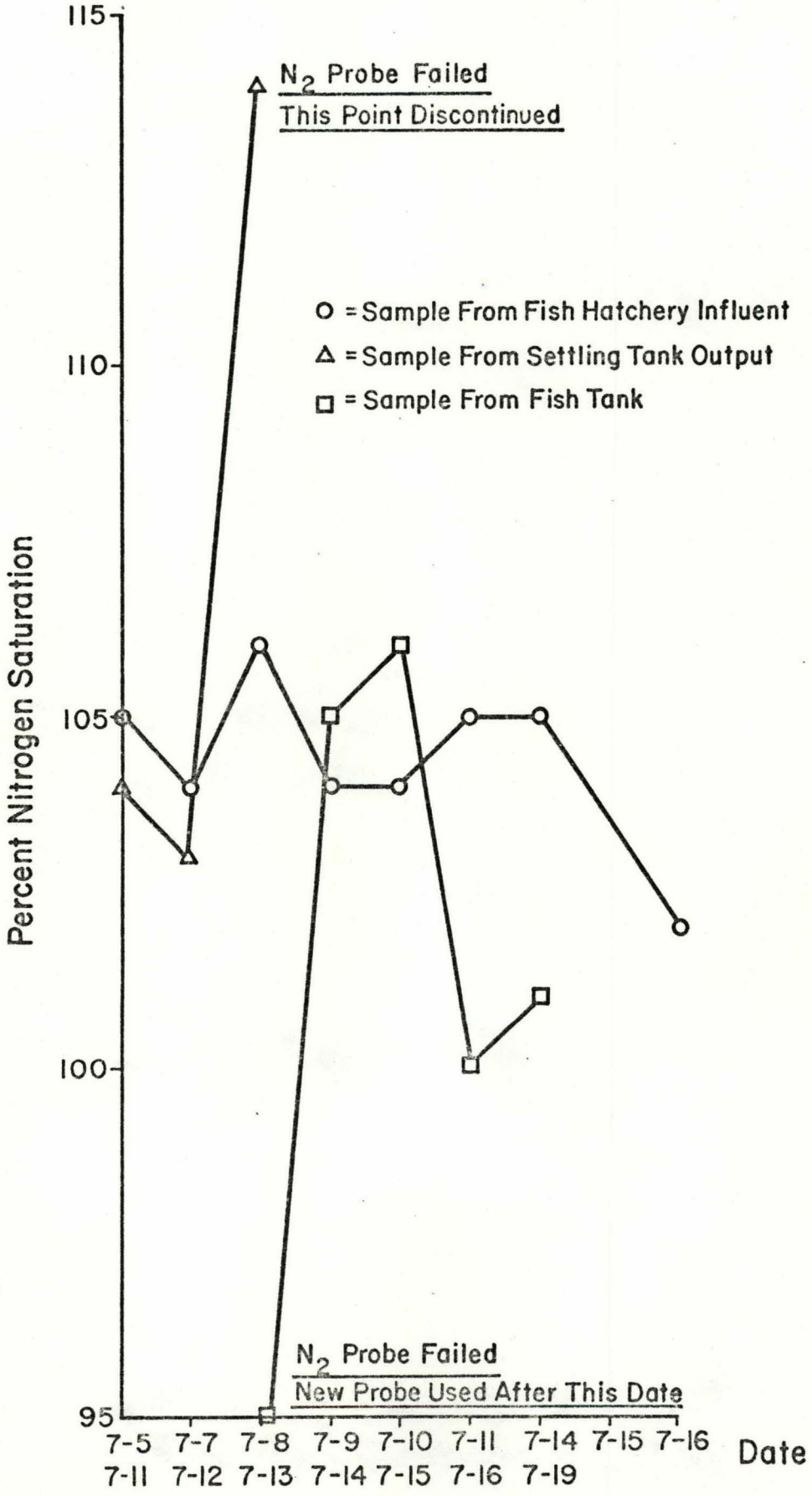


Figure 31
First Gill Arch After 20 Minute
Exposure 0.3 mg/l Ozone

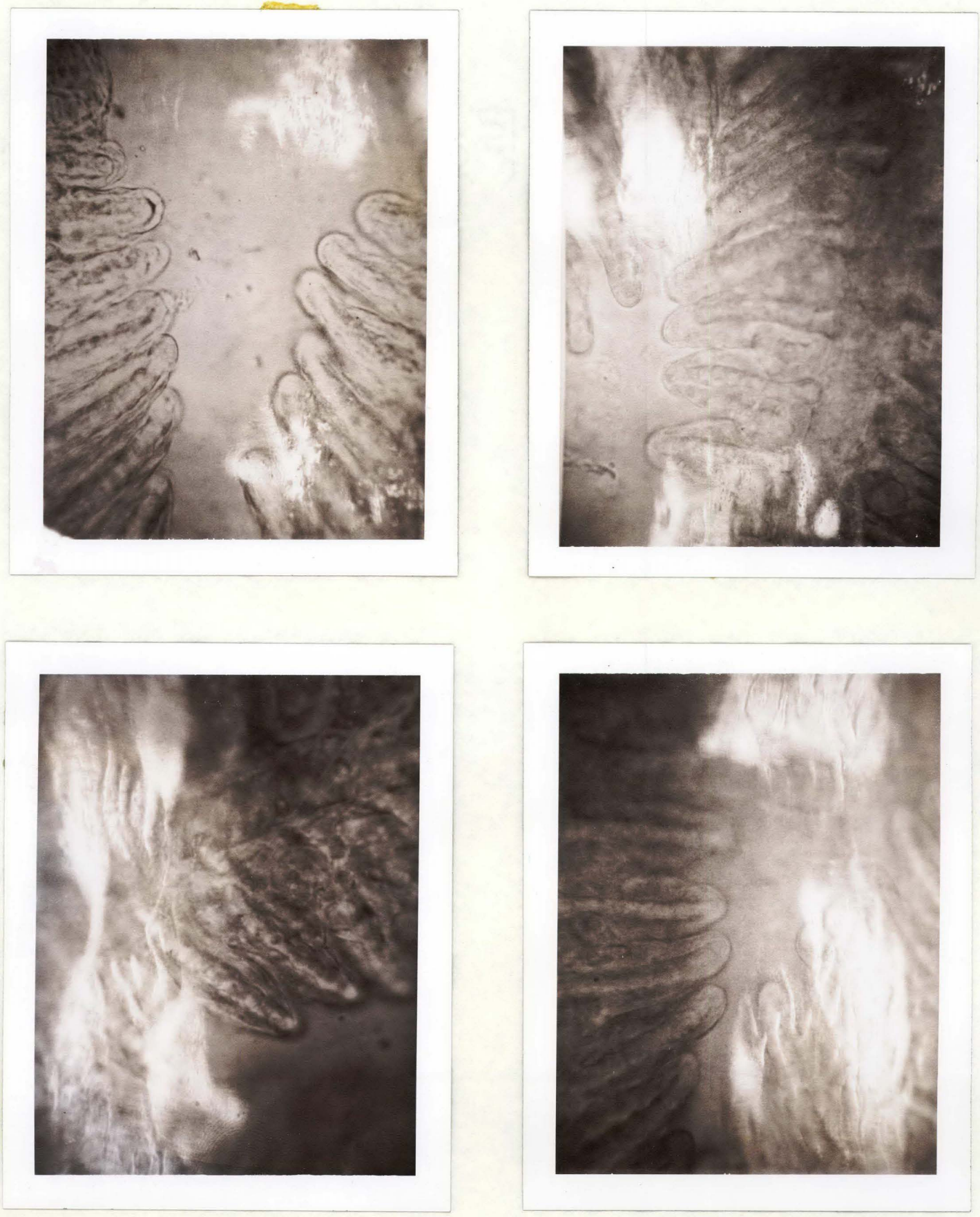


Figure 32
First Gill Arch After 7 Minute
Exposure to 0.3 mg/l Ozone

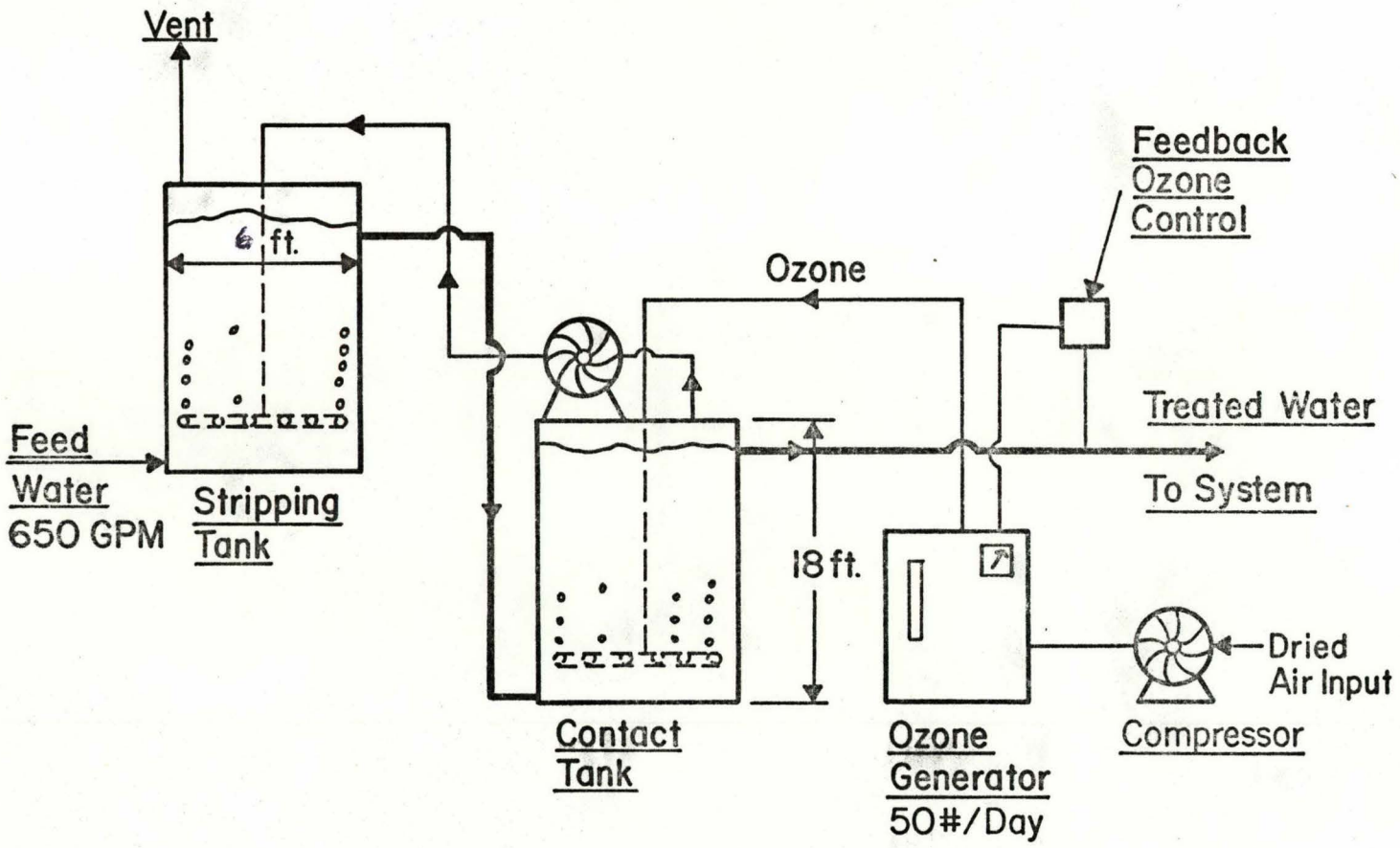


Figure 33. Preliminary Suggested Design:Ozone Treatment System
650 GPM Makeup

APPENDIX A

TABLES

APPENDICES

TABLE I

WELSBACH OZONE GENERATOR CALIBRATION DATA

Run Number	Generator Flowmeter Setting	Volts	Time Seconds	Wet Test Meter-Gas Vol. Measured Ft^3	Gas Volume at STP (Ft^3)	Ml $Na_2S_2O_3$	Ozone Concentration in Gas Mg/l	Ozone Generator Feed Gas
1	0.25	130	72	0.200	.186	42.60	19.4	air
2	0.25	125	73	0.201	.187	41.00	18.6	air
3	0.25	120	80	0.202	.188	43.75	19.7	air
4	0.25	110	87	0.230	.214	41.80	16.6	air
5	0.25	100	85	2.235	.218	39.75	15.5	air
6	0.25	90	127	0.294	.273	32.25	10.0	air
7	0.25	80	150	0.310	.288	11.25	3.3	air
8	0.25	120	106	0.208	.193	40.25	17.7	air
9	0.25	125	75	0.181	.168	38.25	19.3	air
10	0.25	130	61	0.118	.110	44.75	34.5	oxygen
11	0.25	125	48	0.116	.108	42.25	33.2	oxygen
12	0.25	120	74	0.106	.098	41.50	35.9	oxygen
13	0.25	110	102	0.181	.168	45.75	23.1	oxygen
14	0.25	100	83	0.142	.132	46.50	29.9	oxygen
15	0.25	90	85	0.173	.161	41.00	21.6	oxygen
16	0.25	80	197	0.300	.279	17.75	5.39	oxygen
17	0.25	99	143	0.253	.235	42.40	15.3	oxygen
18	0.25	100	-	0.145	.135	38.50	24.2	oxygen
19	0.25	110	88	0.129	.120	42.00	29.7	oxygen
20	0.25	120	100	0.124	.115	43.00	31.7	oxygen

Normality $Na_2S_2O_3$ = 0.1000

Contact Column Volume = 1 Liter

Temperature = 72 Degrees F.

Barometer = 30.0 in. H_2O

Feed Pressure = 9 PSIG

TABLE I (CONT'D)

WELSBACH OZONE GENERATOR CALIBRATION DATA

Run Number	Generator Flowmeter Setting	Volts	Feed Pressure PSIG	Time Seconds	Measured Wet Test Meter-Gas Vol. Ft^3	Gas Volume at STP (Ft^3)	Ml $Na_2S_2O_3$	Barometer MM/Hg	Temperature Degrees F.	Ozone Concent. in Gas Mg/l
1	0.43	115	12.0	1300	0.0978	0.0820	33.4	691.5	69	35.9
2	0.50	115	10.7	73	0.2370	0.1909	79.5	691.5	69	35.3
3	1.08	115	9.0	100	0.1270	0.1020	24.5	686.6	68	20.4
4	1.51	115	9.0	320	0.2160	0.1740	28.0	691.9	68	13.6
5	0.69	115	8.0	250	0.2040	0.1640	54.0	691.9	68	27.8
6	0.25	115	9.4	138	0.1490	0.1200	73.5	691.9	68	51.9
7	0.20	115	8.8	115	0.1060	0.0850	52.0	691.9	68	51.6

Note: Ozone Generator Feed Gas = Oxygen

TABLE II

GRACE OZONE GENERATOR CALIBRATION DATA

Run Number	Generator Flowmeter Setting SCFH	Watts	Volume KI Solution Ml	Barometer Reading MM/Hg	Gas Volume (Wet Test Meter) Ft^3 Measured	STP Gas Volume Ft^3	Ml $Na_2S_2O_3$	Ozone Concentration in Gas Mg/l
1	20	200	1,000	760	0.100	.104	43.00	36.80
2	20	150	1,000	760	0.100	.104	32.75	28.00
3	20	100	1,000	760	0.110	.108	25.50	20.00
4	20	50	1,000	760	0.150	.148	22.80	13.00
5	20	25	1,000	760	0.260	.257	30.20	9.96
6	20	200	1,000	760	0.100	.099	42.00	35.90
7	20	100	1,000	760	0.120	.189	32.75	14.70
8	20	75	1,000	760	0.160	.158	32.75	17.60
9	20	25	1,000	760	0.150	.148	44.00	25.20
10	10	200	800	685.2	0.076	.059	45.50	65.39
11	20	200	1,000	685.2	0.113	.089	40.00	38.09
12	40	200	1,000	685.2	0.130	.102	28.00	23.25
13	60	200	800	685.2	0.160	.126	21.20	14.25
14	80	200	800	685.2	0.202	.158	21.00	11.28
15	90	200	800	685.2	0.200	.157	18.50	9.98

Normality $Na_2S_2O_3$ = 0.1000

Temperature = 68 Degrees F.

Generator Feed Gas = Oxygen

TABLE III

PRELIMINARY LABORATORY TESTS
FOR BACTERIA SURVIVAL
(OZONE CONCENTRATION NOT MONITORED)

Trial Number	Bacteria Type	Ozonation Time Minutes	Survivors Bacteria/Ml	Percent Survivors
1	Bacillus Polymyxas	0	1.5×10^5	
		1/2	6.8×10^4	
		2	9.5×10^4	
		3	8.8×10^4	
		5	1.1×10^4	
		7	4.5×10^2	0.3%
2	Bacillus Polymyxas	0	1.9×10^5	
		1/2	1.8×10^5	
		1	1.8×10^5	
		2	5.6×10^4	
		3	2.0×10^4	
		5	4.7×10^3	2.4%
3	Aeromonas Liquefaciens	0	8.0×10^7	
		1/2	1.3×10^7	
		1	3.6×10^6	
		1.5	2.4×10^6	3.0%
4	ERM	0	2.3×10^8	
		1	3.4×10^5	
		2	6.2×10^4	
		3	4.7×10^3	
		4	0	0%

TABLE IV

LABORATORY DETERMINED OZONE
DECAY CONCENTRATIONS
FOR HALF LIFE CALCULATION

Sample Number	Time (Sec.) After Initial Ozonation	Water Temperature	Ml 0.1N $Na_2S_2O_3$	OTM Test (Cl)	Dissolved Ozone Mg/l	Water Source	Sample Size Ml
1	300	24 °C	-	2.0	1.38	Dworshak Raw Water	
2	800	24 °C	-	1.0	0.69	Dworshak Raw Water	
3	1230	24 °C	-	0.45	0.31	Dworshak Raw Water	
4	1500	24 °C	-	0.35	0.24	Dworshak Raw Water	
5	1800	24 °C	-	0.30	0.21	Dworshak Raw Water	
6	2200	24 °C	-	0.15	0.10	Dworshak Raw Water	
7	2600	24 °C	-	0.10	0.07	Dworshak Raw Water	
1	-0-	25 °C	0.75	-	.46	Tap Water	400
2	900	25 °C	-	2.00	1.38	Tap Water	400
3	1500	25 °C	-	1.75	1.21	Tap Water	400
4	2000	25 °C	-	0.40	.275	Tap Water	400
5	2600	25 °C	-	0.25	.172	Tap Water	400
6	3200	25 °C	-	0.15	.10	Tap Water	400

TABLE IV (CONT'D)

LABORATORY DETERMINED OZONE
DECAY CONCENTRATIONS
FOR HALF LIFE CALCULATION

Sample Number	Time (Sec.) After Initial Ozonation	Absorbance (Shecter Analysis)	Dissolved Ozone Concen. Mg/l	Water Source	Ml $Na_2S_2O_3$	Sample Size Ml	Norm $Na_2S_2O_3$
7	-0-	0.820	7.21	Dworshak Raw Water			
8	30	0.585	5.04	Dworshak Raw Water			
9	60	0.535	4.61	Dworshak Raw Water			
10	90	0.510	4.42	Dworshak Raw Water			
11	120	0.480	4.15	Dworshak Raw Water			
12	180	0.388	3.36	Dworshak Raw Water			
13	240	0.370	3.22	Dworshak Raw Water			
14	300	0.340	2.98	Dworshak Raw Water			
15	360	0.305	2.64	Dworshak Raw Water			
16	420	0.301	2.62	Dworshak Raw Water			
17	-0-		.90	Dworshak Raw Water	1.5	400	.0096
18	30		.60	Dworshak Raw Water	1.0	400	.0096

TABLE IV (CONT'D)

LABORATORY DETERMINED OZONE
DECAY CONCENTRATIONS
FOR HALF LIFE CALCULATION

Sample Number	Time (Sec.) After Initial Ozonation	Dissolved Ozone Concen. Mg/l	Water Source	Ml $Na_2S_2O_3$	Sample Size Ml	Norm $Na_2S_2O_3$
19	60	.54	Dworshak Raw Water	0.90	400	.0096
20	210	.36	Dworshak Raw Water	0.60	400	.0096
21	300	.30	Dworshak Raw Water	0.50	400	.0096
22	-0-	3.75	Dworshak Raw Water	6.25	400	
23	150	3.00	Dworshak Raw Water	5.00	400	
24	300	2.55	Dworshak Raw Water	4.25	400	
25	435	2.25	Dworshak Raw Water	3.75	400	

TABLE V

DILUTION TESTS*
FOR DESTRUCTION OF RESIDUAL OZONE

Test Number	Initial Ml $Na_2S_2O_3$	Dilution	Final Ml $Na_2S_2O_3$	Norm $Na_2S_2O_3$	Dilution Water Source	Hold Time After Dilution, Seconds
1	6.5	1:2	1.75	0.01	Clarifer	0
2	6.5	1:2.5	1.50	0.01	Clarifier	0
3	5.75	1:3.3	0.30	0.01	Clarifier	0
4	5.75	1:5	0.0	0.01	Clarifier	0
5	10	1:5	1.00	0.01	Raw	0
6	10	1:10	0.50	0.01	Raw	0
7	10	1:5	0.90	0.01	Raw	60
8	10	1:10	0.70	0.01	Raw	60
9	10	1:20	0.0	0.01	Raw	60
10	10	1:20	0.0	0.01	Raw	0
11	10	1:10	0.0	0.01	Clarifier	0

*Raw river water is ozonated in contact column. Then it is diluted as indicated, using raw river water.

TABLE VI

TOTAL BACTERIA PLATE COUNTS PRIOR TO AND DURING CONTINUOUS OZONATION - AVERAGE OF THREE PLATES BACTERIA/Ml

Sample Point / Date	UV Light Treatment	Raw River Water	Ozonated Raw Water (Column Outlet)	Water in Pilot Plant Clarifier	Ozonated Recycle Water
5/19/76	1.0	1,260			
5/20/76	1.5	3×10^6			
6/1/76	0.0	29.6			
7/5/76	115.7	1,400	0.3	1,320	
7/6/76	26.6	800	10.6	480	
7/7/76	3.3	230	1.0	465	
7/8/76	41.3	200	3.0	480	
7/9/76	10.6	>1,125	3.6	500	
7/10/76	4.0	>700	2.0	>600	
7/11/76	2.6	184	0.3	600	
7/12/76	6.0	140.7	18.6	>1,000	
7/13/76	3.3	18.0	3.0	533	
7/14/76	2.3	34.3	2.3	800	
7/15/76	14.7	25	2.0	700	
7/16/76	7.7	400	3.0	-	10.7
7/17/76	10.7	-	-	>2,000	2.3
7/18/76	3	-	-	>2,000	1.7
7/19/76	15	-	-	400	4.3

TABLE VII

MILLIPORE TOTAL BACTERIA COUNTS
TAKEN DURING CONTINUOUS
OZONATION BACTERIA/Ml

Sample Point	UV Light Treatment	Raw River Water	Ozonated Raw Water (Column Outlet)
Date			
7/5/76	9.5	49.5	0.5
7/6/76	10.5	32.5	1.5
7/7/76	1.5	95.0	1.5
7/8/76	3.0	500.0	1.5
7/9/76	0.5	TNTC*	3.0
7/11/76	4.0	TNTC	1.0
7/12/76	8.5	TNTC	5.5
7/13/76	5.0	TNTC	0
7/14/76	58.0	-	0

*Too numerous to count

TABLE VIII

PILOT PLANT
STARTUP AND APPROACH TO STEADY STATE
BEFORE OZONE

Sample Point*	Date	BOD Mg/l	NO_2 Mg/l	NO_3 Mg/l	NH_3 Mg/l	T.O.N. Mg/l	Suspended Solids (4×10) Mg/l	Alkalinity Mg/l	ph
	6/2/76								
1		5.5	.26	1.15	1.15	2.2	80	22.4	6.9
2		4.9	.26	1.15	1.05	1.8	34	19.6	6.4
4		3.9	.26	1.30	1.00	2.2	80	19.6	6.5
Clarifier sludge						35.7	715		
	6/4/76								
1		16.4	.11	1.30	1.70	12.3	45	16.8	6.6
2		5.0	.11	1.10	1.55	1.8	4.0	22.4	6.8
4		2.3	.12	1.60	0.90	2.5	7.0	19.6	6.7
Clarifier sludge						22.2	310		
Tower Out						1.2	168		
	6/7/76								
1		2.2	.05	1.50	0.95	0.9	11	16.8	6.8
2		3.0	.05	1.35	0.90	0.9	2.0	16.8	6.6
4		2.5	.05	1.60	0.65	0.6	11	16.8	6.7
Clarifier sludge						12.8	160		
	6/9/76								
1		10.0	.06	1.40	1.65	2.8	19	19.6	6.8
2		9.2	.065	1.40	1.30	2.2	14	16.8	6.6
4		5.9	.07	1.45	1.00	1.7	9.0	16.8	6.6
Clarifier sludge						38.2	410		

*Sample Point 1 = fish tank effluent a clarifier inlet
Sample Point 2 = clarifier effluent
Sample Point 4 = treated water influent to fish tanks
Clarifier sludge = clarifier sludge basin
Tower out = biofilter treatment tower sludge drain line

TABLE VIII (CONT'D)

PILOT PLANT
STEADY STATE CONDITIONS OF PILOT PLANT
BEFORE OZONE

Sample Point	Date	BOD Mg/l	NO_2 Mg/l	NO_3 Mg/l	NH_3 Mg/l	T.O.N. Mg/l	Suspended Solids ($\times 10^4$) Mg/l	Alkalinity Mg/l	ph
	6/11/76								
1		3.6	.025	0.3	1.00	1.2	30	19.6	6.7
2		4.4	.025	0.9	1.10	1.8	27	19.6	6.7
4		4.5	.030	0.6	0.80	0.9	23	19.6	6.5
Clarifier sludge						81.3	512		
Tower Out							248		
	6/13/76								
1		6.3	.010	0.5	0.80	1.5	6.0	19.6	6.7
2		3.6	.010	0.8	0.75	2.5	2.0	19.6	6.7
4		3.0	.010	0.7	0.70	0.9	2.0	19.6	6.8
Clarifier sludge						67.8	587		
	6/15/76								
1		5.7	.017	0.7	0.60	0.6	11	14.0	6.2
2		4.8	.015	0.8	0.80	-	0.0	19.6	6.4
4		1.8	.018	0.9	0.60	0.9	6.0	16.8	6.5
Clarifier sludge						73.9	353		
	6/16/76								
1		12.9	.022	1.1	1.10	10.2	17	25.2	6.9
2		13.2	.022	0.9	0.75	2.8	8.0	22.4	6.9
4		7.3	.020	1.2	0.75	1.8	4.0	22.4	6.8
Clarifier sludge							947		

TABLE VIII (CONT'D)

PILOT PLANT CONDITIONS
DURING INTERMITTENT OZONATION
TRIAL RUNS

Sample Point	Date	BOD Mg/l	NO_2 Mg/l	NO_3 Mg/l	NH_3 Mg/l	T.O.N. Mg/l	Suspended Solids ($X 10^4$) Mg/l	Alkalinity Mg/l	ph
	6/18/76								
1		4.6	.123	1.6	1.25	2.9	9.0	22.4	6.9
2		6.4	.115	1.4	1.10	2.3	7.0	19.6	6.8
4		5.0	.128	1.5	1.05	4.8	7.0	19.6	6.7
Clarifier sludge						218.1	625		
Tower sludge						6.2	35.5		
	6/19/76								
1			.035	0.95	1.2				
2			.05	1.15	0.85				
4			.05	1.30	0.85				
Clarifier sludge									
	6/21/76								
1		4.7	.022	0.85	0.85	1.8	6.0	19.6	6.6
2		3.5	.021	0.80	0.80	1.8	5.0	19.6	6.5
4		1.5	.023	0.90	0.70	15.4	7.5	19.6	6.3
Clarifier sludge						200	835		
	6/23/76								
1		13.5	.018	0.65	0.62	2.5	4.0	25.2	6.4
2		8.6	.016	0.60	0.75	1.5	4.0	28.0	6.7
4		4.8	.020	0.70	0.60	2.3	4.0	25.2	6.8
Clarifier sludge						24.6	182		

TABLE VIII (CONT'D)

PILOT PLANT CONDITIONS
DURING INTERMITTENT OZONATION
TRIAL RUNS

Sample Point	Date	BOD Mg/l	NO_2 Mg/l	NO_3 Mg/l	NH_3 Mg/l	T.O.N. Mg/l	Suspended Solids (4×10) Mg/l	Alkalinity Mg/l	ph
	6/25/76								
1		12.3	.030	1.4	0.55	2.8	11	25.2	6.6
2		8.0	.028	1.4	0.60	2.2	6.0	22.4	6.5
4		4.3	.045	1.2	0.65	1.5	4.0	22.4	6.4
Clarifier sludge						68.4	277		
Tower Out						7.2	96		
	6/28/76								
1		3.2	.030	1.2	0.6	1.8	10	36.4	6.8
2		3.6	.025	1.0	0.6	2.2	12	39.2	6.7
4		3.6	.030	0.9	0.4	2.8	9.5	39.9	6.7
Clarifier sludge						53.6	347		

TABLE VIII (CONT'D)

PILOT PLANT CONDITIONS
DURING CONTINUOUS OZONE RUN

Sample Point	Date	BOD Mg/l	NO_2 Mg/l	NO_3 Mg/l	NH_3 Mg/l	T.O.N. Mg/l	Suspended Solids ($X\ 10^4$) Mg/l	Alkalinity Mg/l	ph
	7/5/76								
1		6.4	.05	2.0	.4	3.7	3.0	16.8	6.8
2		6.2	.04	1.9	.3	2.77	1.7	14.0	6.8
4		4.7	.05	1.8	.3	2.5	3.7	14.0	6.8
Clarifier sludge						44.4	246		
	7/6/76								
1		6.2	.055	2.7	.5	2.2	7.3	16.8	6.8
2		5.2	.05	2.3	.45	2.2	6.7	14.0	6.7
4		5.0	.05	2.6	.5	1.8	2.7	16.8	6.3
Clarifier sludge						46.2	256		
	7/7/76								
1		4.6	.035	3.5	.6	2.5	2.7	14.0	6.8
2		4.8	.033	2.9	.4	2.2	1.7	16.8	5.8
4		5.9	.030	3.5	.3	1.7	4.0	16.8	6.9
Clarifier sludge						49.3	550		

TABLE VIII (CONT'D)

PILOT PLANT CONDITIONS
DURING CONTINUOUS OZONE RUN

Sample Point	Date	BOD Mg/l	NO_2 Mg/l	NO_3 Mg/l	NH_3 Mg/l	T.O.N. Mg/l	Suspended Solids ($X\ 10^4$) Mg/l	Alkalinity Mg/l	ph
	7/8/76								
1		4.3	.028	3.1	0.5	2.00	9.0	11.2	6.8
2		5.3	.025	2.8	0.5	2.156	5.0	16.8	6.6
4		5.7	.033	3.0	0.3	2.31	3.0	14.0	6.9
Clarifier sludge						20.94	246		
	7/9/76								
1		4.4	.05	2.9	.80	2.46	7.0	14.0	6.8
2		6.3	.04	2.5	.75	2.00	9.0	14.0	6.8
4		6.2	.045	2.6	.60	1.85	5.0	11.2	6.8
Clarifier sludge						22.79	116		
Tower Out									
				- Air Run -					
	7/13/76								
1		.033	2.5	0.75					
2		4.8	2.5	0.60					
4		1.8	2.4	0.50					
Clarifier sludge									

TABLE VIII (CONT'D)

PILOT PLANT CONDITIONS
DURING CONTINUOUS OZONE RUN

Sample Point	Date	BOD Mg/l	NO_2 Mg/l	NO_3 Mg/l	NH_3 Mg/l	T.O.N. Mg/l	Suspended Solids (4 (X 10)) Mg/l	Alkalinity Mg/l	ph
	7/14/76								
1		7.2	.043	2.4	0.5	1.85	25		
2		7.1	.037	2.0	0.4	2.16	21		
4		6.3	.043	2.4	0.3	1.85	16		
Clarifier sludge						48.70	33		
	7/15/76								
1			.027	1.8	0.5				
2			.030	2.0	0.6				
4			.030	2.1	0.5				
Clarifier sludge									
	7/16/76								
1		5.4	.033	2.5	0.8	2.46	20	16.8	6.8
2		5.3	.025	2.5	0.7	2.31	15	16.8	6.8
4		3.6	.035	2.5	0.6	1.54	11	16.8	6.8
Clarifier sludge						68.30			
Tower Out						8.62			
	7/19/76								
1		4.9	0.08	2.1	0.9	2.31		16.8	7.0
2		5.2	0.08	2.8	0.7	2.31		16.8	6.8
4		5.6	0.09	2.8	0.9	1.69		16.8	6.8
Clarifier sludge						65.30			

TABLE IX

PERCENT DISSOLVED NITROGEN CONCENTRATION

Date	Biofilter Pilot Plant Clarifier	Biofilter Pilot Plant Cuthroat Fish Tank	Fish Hatchery Influent
7/5/76			105
7/6/76			104
7/7/76			106
7/8/76			104
7/9/76			104
7/10/76			105
7/11/76	104		105
7/12/76	103		102
7/13/76	114 (Probe Failure)	95 (Probe Failure)	
7/14/76		105	
7/15/76		106	
7/16/76		100	
7/19/76		101	

TABLE X

CONTINUOUS RUN
CONTACT COLUMN RESIDUAL OZONE - DELIVERED TO CLARIFIER*

Date	Time	Ml $Na_2S_2O_3$	Residual Ozone Mg/l	Comments
7/2/76	5:30 PM	0.2	0.12	75 volts
7/3/76	1:00 PM	0.0	0.00	Need to reset 80 volts
	2:00 PM	0.2	0.12	80 volts
7/4/76	3:00 PM	0.2	0.12	" "
7/5/76		0.2	0.12	" "
7/6/76		0.2	0.12	" "
7/7/76		0.2	0.12	" "
7/8/76		0.3	0.18	" "
7/9/76		0.4	0.24	Water flow down - reset to 3.3 GPM
	3:00 PM			Switched from 0 to air feed gas. Volts to 100
	3:50 PM	1.5	0.96	Reset volts to 90
	4:00 PM	0.4	0.24	Volts to 85
	5:00 PM	0.2	0.12	
7/10/76	1:30 PM	0.0	0.00	Volts to 90
	2:15 PM	0.5	0.30	Volts to 88
	2:45 PM	0.2	0.12	88 Volts
7/11/76	1:30 PM	0.1	0.06	" "
7/12/76				Neglected to record residual data
7/13/76		0.3	0.18	88 Volts
7/14/76		0.2	0.12	" "
7/15/76		0.3	0.18	" "

*Normality $Na_2S_2O_3$ = 0.01

TABLE X (CONT'D)

CONTINUOUS RUN
CONTACT COLUMN RESIDUAL OZONE - DELIVERED TO CLARIFIER

Date	Time	Ml $Na_2S_2O_3$	Residual Ozone Mg/l	Comments
7/16/76	12:30 PM	0.01	0.06	Switched O_3 treatment from makeup to recycle after sampling
	3:00 PM	0.00	0.00	Volts to 110 Volts to 120
	3:30 PM	1.20	0.72	Volts to 115
	4:00 PM	1.20	0.72	Volts to 110
	4:30 PM	2.00	1.20	Water flow erratic--increased
	5:00 PM	0.90	0.54	Water flow increased
	5:30 PM	0.50	0.30	Water flow stable
	6:00 PM	0.60	0.36	Volts to 105
	6:30 PM	0.60	0.36	Volts to 100
	7:00 PM	0.60	0.36	Volts to 95
	7:30 PM	0.10	0.06	Volts to 91
7/17/76	2:00 PM			Air cylinders empty-- regulator replaced - 90 volts
	3:00 PM	0.00	0.00	Volts to 95
	3:30 PM	0.00	0.00	Volts to 100
	4:00 PM	0.00	0.00	Volts to 110
	4:30 PM	0.00	0.00	Volts to 120
	5:00 PM	0.00	0.00	Volts to 130
	5:30 PM			Volts reset to 90
	6:00 PM	1.00	0.06	Volts to 85
	6:30 PM	0.00	0.00	Volts to 80
	7:00 PM	0.00	0.00	Volts to 95

TABLE X (CONT'D)

CONTINUOUS RUN
CONTACT COLUMN RESIDUAL OZONE - DELIVERED TO CLARIFIER

Date	Time	Ml $Na_2S_2O_3$	Residual Ozone Mg/l	Comments
7/18/76	2:30 PM	0.00	0.00	Volts to 120
	3:00 PM	0.00	0.00	Volts to 125
	3:15 PM	0.00	0.00	Volts to 125
	4:00 PM	0.00	0.00	Volts to 130
	4:30 PM	0.70	0.42	Volts to 128
	5:00 PM	0.80	0.48	Volts to 127
	5:30 PM	0.70	0.42	Volts to 125
	5:45 PM	0.60	0.36	Volts to 125
	6:00 PM	0.30	0.18	Volts at 125
	6:30 PM	0.30	0.18	Volts at 125
	7:00 PM	0.30	0.18	Left at 125 volts for night
7/19/76	4:00 PM	2.10	1.26	System shutdown-- Nitrifying bacteria shocked

TABLE XI

CONTINUOUS RUN
RESIDUAL OZONE - COLUMN OUT

Number	Water Flow GPM	Gas Flow SCFH	Power Watts	Ml $Na_2S_2O_3$	Residual Ozone Mg/l
Normality $Na_2S_2O_2$ = 0.0100					
1	2	20	200	9.25	5.55
2	4	20	200	10.10	6.06
3	6	20	200	6.50	3.90
4	8	20	200	7.50	4.50
5	10	20	200	6.00	3.60
6	2	20	200	10.00	6.00
7	10	20	200	6.50	3.90
8	2	20	200	8.50	5.10
9	2	20	150	7.50	4.50
10	2	20	100	6.00	3.60
11	2	20	50	3.20	1.92
12	2	20	25	0.50	0.30
13	4	20	25	0.25	0.15
14	4	20	50	1.00	0.60
15	4	20	100	3.00	1.80
16	4	20	150	5.60	3.36
17	4	20	200	6.25	3.75
18	4	20	200	9.50	5.70
19	8	20	200	8.50	5.10
20	8	20	150	7.00	4.20
21	8	20	100	5.00	3.00
22	8	20	50	1.80	1.08
23	8	20	25	1.00	0.60
24	10	20	200	7.00	4.20
25	10	20	150	5.50	3.30
26	10	20	100	3.25	1.95
27	10	20	50	1.50	0.90
28	10	20	25	0.80	0.48
29	4	50	200	6.50	3.90
30	4	50	150	4.50	2.70
31	4	50	100	2.30	1.38
32	4	50	50	0.75	0.45
33	4	20	200	9.50	5.70
34	4	20	150	8.00	4.80
35	4	20	100	5.25	3.15
36	4	20	50	1.50	0.90
Normality $Na_2S_2O_3$ = 0.0094					
37	2	10	15	1.50	0.90
38	2	10	25	4.75	2.85
39	2	10	50	7.50	4.50
40	2	10	100	13.25	7.95
41	2	20	100	7.25	4.35
42	2	20	50	3.00	1.80
43	2	20	25	2.50	1.50
44	2	20	10	0.00	0.00
45	5	20	15	0.25	0.15
46	5	20	25	0.25	0.15
47	5	20	50	2.50	1.50
48	5	20	100	6.50	3.90
49	5	20	150	9.25	5.55
50	5	20	200	11.50	6.90
51	5	10	200	14.00	8.40
52	5	10	150	13.00	7.80
53	5	10	100	10.50	6.30
54	5	10	50	2.60	1.56
55	5	10	25	1.10	0.66

Note: Sample Volume = 1 Liter

APPENDIX B
CHRONOLOGICAL ACCOUNT
OZONE PILOT PLANT
CONTINUOUS OPERATION

June 1st through June 16: Biofilter pilot plant operated undisturbed to collect steady state operating data.

June 16 through June 18: Started integrated pilot plant on first continuous trial run. Grace ozone unit is used with oxygen as feed gas. Operating conditions were:

2 GPM makeup water flow rate

1 mg/l residual ozone out of contact column

System was monitored on June 16 for residual ozone, none was detected. On June 17, approximately 0.15 mg/l ozone was detected throughout the biofilter system. The fish appeared under no stress, so the system was allowed to continue in operation. On the 18th, the measured ammonia and NO_2 levels drastically increased (see Figure 21), indicating the nitrifying bacteria had been shocked or killed. The ozone generating unit was shutdown and the system flushed with hatchery water. The biofilter was reseeded with nitrifying bacteria. At no time did fish mortalities occur or did the fish appear to be stressed. Residual levels remained at 0.15 mg/l until shutdown.

The 0.15 mg/l residual ozone level measured throughout the system on the 17th and 18th came as a complete surprise. Batch tests had indicated that all residual ozone would be very rapidly destroyed in the system at this point. A

different approach to finding residual ozone levels was adopted. Using the rate data collected in the laboratory, a mass balance was applied to the system to determine if residual ozone was predicted at a steady state condition. It was assumed that the biofilter pilot plant was a continuous flow stirred tank reactor (see calculation Appendix D). A residual ozone concentration of .008 mg/l was predicted for the system. This confirmed the batch test that no measurable residual should be in the system. It was decided to continue with the pilot plant run using a 0.1 mg/l residual. It was felt that this reduction in the feed would reduce the residual in the system by the same amount, to 0.01 mg/l.

June 24 through June 26: The ozone pilot plant was started, feeding makeup water into the pilot plant with 0.2 mg/l residual ozone at 2 GPM. No residual ozone was measured in the system, however on June 25 the pH which was being monitored fell to 5.8. On the 26th, the pH fell to 5.6 and soda ash was added to the system. After an hour the pH was noted to be increasing and more soda ash was added to the system. The pH than rapidly rose to 8.9 and the fish started showing signs of stress. The system was immediately shutdown and flushed with hatchery water. No fish fatalities occurred and after the problem was corrected, the fish showed no further signs of stress.

Investigation showed the pH meters to give erroneous readings. Three separate meters were tried and all failed

within a day or two. pH was no longer determined using meters after this. Laboratory determined alkalinity was used as the primary method of measurement.

The biofilter pilot plant has not been sterilized by this problem and when placed back on recycle after flushing it rapidly returned to steady state. As a result, the ozone generator was restarted on the following day.

June 27 through July 2: The ozone generator was restarted on June 27 and on June 28 power fluctuations were noted on the watt meter of the generator. Varying levels of residual ozone out of the contact column were also noted. Attempts were made to correct the fluctuations by varying the power to the generator on the 28th and 29th. On the 29th the manufacturer of the generator, Union Carbide, was contacted and recommended replacement of a diode. This was replaced on the 30th and the unit appeared to be functioning normally. On the following day, July 1, the main fuse in the unit blew out. Replacement of the main fuse only caused it to blow again. The makeup water from the ozone pilot plant was turned off and the unit returned to University of Idaho for repairs. These repairs were not completed in time to use this generator again in the pilot plant.

July 2 through July 9: Pilot plant restarted using the Welsbach ozone generator. The pilot plant operated normally during this time with no problems. The feed gas to the generator was oxygen. During this time the ozone generator needed virtually no adjustments. See Table X for parameters used.

July 9 through July 16: Feed gas changed to air. Power had to be increased slightly to account for lower concentration of oxygen, as was expected. System rapidly returned to steady state and operated unattended except to change tanks. Dissolved nitrogen levels were monitored, but the probe quickly failed after obtaining only a few readings. Dissolved nitrogen was not monitored after this.

The lack of time remaining for the study required that the makeup water treatment run be discontinued after only two weeks. The ozone pilot plant was then realigned to treat 10% of the recycle water, 3 GPM.

July 16 through July 19: Difficulty was noted in obtaining a steady state condition of residual ozone on July 16. It was decided to leave the plant operating on the same power as the makeup water treatment run for a day to see if it would steady out. On July 17 and 18 full days were spent trying to obtain a steady state condition of residual ozone levels at the column outlet. The system was set to a higher power level than used for makeup treatment, late on the 18th. It was then left overnight to see if a steady state condition could be reached. Before leaving residual level was checked at the column outlet and was approximately 0.2 mg/l.

The following day the measured residual at the column outlet was 1.3 mg/l. The system was shutdown, and the biofilter pilot plant flushed out. Ammonia and nitrate tests later verified that the biofilter nitrifying bacteria

had been killed. It was decided, due to control problems with the recycle water to discontinue this test.

Since it was required that the pilot plant be removed from the fish hatchery by the end of July it wa decided to go directly into the mortality study. For ths trial, the ozone pilot plant was retained in recycle configuration and the large fish were removed from the system. The ozone pilot plant was retained in recycle configuration for two reasons. First, it was already in that configuration and second, it gave the ability to increase water flow through the ozonation column without increasing water flow through the plant. The large fish were released because they produced the majority of the ammonia in the pilot plant. The nitrifying bacteria were put out of commission in the previous excursions before any other changes were noted. It was felt that with the nitrifiers out of commission, ammonia levels would rapidly increase to the point of causing stress and mortalities. This would cause interference with the ozone test. The steelhead fry produced virtually no ammonia, compared to the system volume. Therefore, even with the nitrifiers out, the ammonia would remain below stress levels. It was then decided to run this test with only the steelhead fry in the system.

Approximately twenty of the steelhead fry were removed at this time and dissected. They were examined primarily for gill damage. Figure 17 shows random selections of these sections. No damage to the gill can be discerned, other

than that present at the start of the study. Clubbing and edema is evident, however, these fish were still considered very healthy for recycle hatchery fish. Five of these fish were preserved for further histological workup. No affects of ozone were noted.

July 22 through July 24: The ozonation column was initially set for 9 GPM and a residual out of 2.4 mg/l ozone. During the date of July 22, no residual ozone was detected in the system. At this time the makeup water was turned off and the system was placed on total recycle. The pump reservoir tank was also intentionally short circuited, by addition of a pipe directly to the pump inlet, to reduce residence time in the system. During the day of July 23, pipes were added to the weirs to eliminate splash, thereby reducing possible stripping. A very strong odor of ozone was noted at the clarifier, by the column inlet. Ozone concentration had built up in the clarifier during the day to 0.2 mg/l. None was detected elsewhere in the system. The fish showed no signs of stress.

During the day of July 23, the clarity of the water in the system markedly increased. Prior to this test the water was fairly clear, but by the end of the day the water had become literally "crystal clear." Fungal growths in the clarifier were also noted to be partially bleached white.

On the morning of July 24 no residual ozone was noted in the fish tank. The clarifier contained 0.4 mg/l residual ozone and only a trace amount could be found in the pump

reservoir. The system was allowed to run until 12 noon, when it was checked and no residual ozone was in the fish tank. At this time the system was temporarily shutdown and the majority of the steelhead fry released. It was felt that the test had obtained its objective in determining the extent of an ozone accident that could be tolerated.

To determine the cause of death of the fry, and the extent of a dose which can be tolerated, approximately 100 steelhead fry were retained in the system. The tank which was used as the larger fish tank was connected directly to the ozone column outlet and ozonated to a residual of 0.3 mg/l. Twenty fish were introduced to this tank. When checked again twenty minutes later all fish were dead. A second group of sixteen fish was introduced to the tank and watched carefully. At four minutes the fish showed signs of stress, at eight minutes the first mortality occurred, at eleven minutes 50% mortality occurred and at fourteen minutes 100% mortality occurred. Ten of each group of fish were dissected and five of each group were sent for a complete histological exam.

The following day the ozone pilot plant was returned to the University of Idaho. The biofilter pilot plant was dismantled by Dworshak operating personnel.

APPENDIX C
SAMPLE CALCULATION
OZONE CONCENTRATION IN GAS LEAVING OZONE GENERATOR

1. Oxygen feed to generator: (Data from Table II, Run 1)

Data (measured): Gas volume: 0.10 $Ft.^3$
KI volume: 1 liter
Ml $NA_2S_2O_3$: 43.00

Norm. $Na_2S_2O_3$: 0.10
Temperature: 68 Degrees F.
Barometer: 29.95 lN Hg

Correction of gas volume to STP:

$$V_{STP} = \left(\frac{PMEAS.}{P_{STP}}\right)\left(\frac{TSTP}{T_{MEAS}}\right) V_M$$

$$V_{STP} = \left(\frac{29.95}{29.92}\right)\left(\frac{528}{508}\right) 0.10$$

$$V_{STP} = .104\ Ft^3 = 2.94 \text{ liter}$$

Calculation of quantity of ozone measured:

$$Mg\ O_3 = \left(\frac{Ml\ NA_2S_2O_3 \times Normality \times 24{,}000}{\text{Sample Vol. Ml}}\right) \times 1 \text{ liter sample}$$

$$Mg\ O_3 = \frac{43 \times 0.1 \times 24{,}000}{1000} \times 1$$

$$= 103.2\ Mg\ O_3$$

Concentration in gas at STP:

$$CONC. = \frac{\text{Quantity } O_3}{\text{Volume Gas}}$$

$$= \frac{103.2 \text{ Mg}}{2.94 \text{ liter}} = 35.1 \text{ Mg/l } O_3$$

2. Air generating gas: (Data from Table 1, Run 1)

Data (measured): Gas volume: 0.20 Ft^3
Kl volume: 1 liter
Ml $Na_2S_2O_3$: 42.60
Norm. $Na_2S_2O_3$: 0.10
Temperature: 70 Degrees F.
Barometer: 30.06 In. Hg

Correction of gas volume to STP:

$$V_{STP} = \left(\frac{PMEAS}{P_{STP}}\right)\left(\frac{TSTP}{T_{MEAS}}\right) V_M$$

$$V_{STP} = \left(\frac{30.06}{29.92}\right)\left(\frac{492}{532}\right) 0.20$$

$$V_{STP} = .186\ Ft.^3 = 5.26 \text{ liters}$$

Calculation of quantity of ozone measured:

$$Mg\ O_3 = \frac{Ml\ Na_2S_2O_3 \times Norm. \times 24{,}000}{\text{Sample Vol. Ml}} \times \frac{1 \text{ liter}}{\text{sample}}$$

$$Mg\ O_3 = \frac{42.60 \times 0.10 \times 24{,}000}{1000} \times (1)$$

$$= 102.24\ Mg\ O_3$$

Concentration ozone in gas at STP:

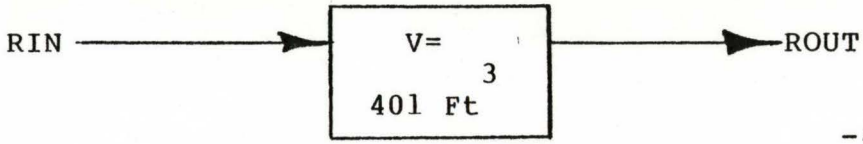
$$CONC. = \frac{\text{Quantity } O_3}{\text{Volume Gas}}$$

$$= \frac{102.24\ Mg}{5.26 \text{ liter}} = 19.4\ Mg/l$$

APPENDIX D

Sample Calculation:

OZONE MASS BALANCE ON INTEGRATED PILOT PLANT



Rate in = 1 Mg/l @ 2 Gal/min = 1.58×10^{-4} gm-mole/min

Rate out = (CONC. $[O_3]$ in system) (flow rate) gm-mole/min

Rate of consumption = Ko [CONC. $[O_3]$ in system] (System Volume)

$[O_3]$ = Total moles of ozone V = System Volume $401\ Ft^3$, Ko = $\frac{.693}{8\ min} = .087\ min^{-1}$

At Steady State:

RIN - ROUT = RCON

$$(1.58 \times 10^{-4}) - [O_3]\frac{V\ flow}{V\ sys} - V(Ko)\frac{[O_3]}{V} = 0$$

$$(1.58 \times 10^{-4}) - [O_3]\frac{(.267)\frac{Ft^3}{Min}}{401} - \frac{[O_3]}{401}(401\ Ft^3)(.087) = 0$$

$$(1.58 \times 10^{-4}) - (6.65 \times 10^{-4})[O_3] + .087[O_3]$$

1.8×10^{-3} = moles in system

1.58×10^{-7} = mole/l

.008 mg/l predicted residual

APPENDIX E
OZONE SYSTEM
PRELIMINARY DESIGN
COST ANALYSIS

Basis

1. Makeup water flow rate = 650 GPM

2. Maximum ozone required = 3 mg O_3 /liter water

3. Two contact chambers, five minutes retention time in each chamber. Counter-current contacting. First tank primarily used for stripping ozone out of vent gases (see Figure 33).

4. Feed gas to ozonator is air.

CALCULATIONS - PRELIMINARY DESIGN

1. 3 mg/l delivered to 650 GPM = 23 lbs/day ozone

2. Total air flow rate to contact chambers: absorption approxiamtely 60% efficient

$$\frac{23 \text{ lbs/day}}{0.60} = 38 \text{ lbs/day ozone generated}$$

$$= 12 \text{ Ft}^3/\text{Hr pure ozone at STP}$$

Generator produces 1% by volume ozone:

$$\frac{12 \text{ Ft}^3/\text{Hr}}{0.01} = 1{,}200 \text{ Ft}^3/\text{Hr at STP total air flow rate}$$

3. Contact chambers (two each)

650 GPM, 5 min retention time (for liquid)

1,200 Ft^3 /Hr air (STP)

6 Ft x 18 Ft high x 3/16 wall stainless steel tank (includes three foot clearance at top)

Capital Equipment (1977 Costs)	Direct Cost $
1. Ozone generator, 50#/day-package unit with air dryer and compressor (FOB plus 15% installation cost) [18]	74,200
2. Two each 3,800 gallon stainless steel tanks, 6' x 18' x 3/16 wall, domed 1 end [19]	9,500 (each)
3. 1,200 Ft^3/Hr Blower (STP) [20]	2,200
4. Ozone/Liquid mixing Devices--Two Required	3,500
5. Special Ozone Instrumentation and Alarms	5,000
Total Direct Cost	103,900
Indirect Cost (34% of Direct Cost)	35,000
Total Direct and Indirect Cost	138,900
Contingency and Contractors' Fee (18% of D and I Cost)	25,000
Total Capital Investment	$163,900
Annual Cost (365 days/year)	$/year
Electricity 10 KW-HR/LB Ozone (at 2.2 cents /KW-HR)	4,015
Operating Labor	1,500
Maintenance and Repairs (3% of Direct Cost)	3,117
Depreciated (20 year life)	8,195
Total Cost:	$16,827/year

APPENDIX F
ULTRAVIOLET SYSTEM
PRELIMINARY DESIGN
COST ANALYSIS

Basis

1. Makeup water flow rate = 650 GPM

2. Ultraviolet contacting system identical to existing installations at Dworshak

   Serpentine contactors supplied by Aquafine Corporation. Supplied system incldues all electrical controls and safety devices.

Capital Equipment (1977 Costs)	Direct Cost $
1. Ultraviolet contactor, complete with valves and instrumentation [17] (F.O.B PLUS 50% installation cost)	57,000
Total Direct Cost	57,000
Indirect Cost (34% of Direct)	19,400
Total Direct and Indirect Cost	76,400
Contingency and Contractors Fee (18% of D and I Cost)	13,750
Total Capital Investment	$90,150

Annual Cost (365 days/year)	$/year
Electricity (4 KW at 2.2¢/KWHR)	770
Operating Labor	1,500
Maintenance	
Lamp Cleaning (4 times/year)	350
Relamping (2 times/year	3,200
Miscellaneous (3% of direct cost)	1,710
Depreciation	4,500
Total Cost	$12,030/year