

ZERO DISCHARGE PROGRAM
AT AN UNCOATED GROUNDWOOD PAPER MILL

BY

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EXECUTIVE SUMMARY

In July, 1990, Hennepin Paper Company implemented a program aimed at eliminating the discharge of industrial wastewater to the Mississippi River. A wastewater recycling system comprised of pumps, surge tank and filtration system has reduced total discharges 82 percent. Pollution prevention achieved includes the annual elimination of 562 million gallons of wastewater, 149,000 pounds of total suspended solids, and 57,000 pounds of biochemical oxygen demand.

INTRODUCTION

Hennepin Paper Company, an uncoated groundwood paper mill in Little Falls, Minnesota, manufactures primarily colored Construction Paper using groundwood pulp (Aspen), kraft pulp, and wastepaper. The mill is located on the West bank of the Mississippi River and has historically relied on the River as the primary source for incoming process water. As a result, thousands of gallons of process and cooling wastewater have been discharged on a daily basis.

Hennepin Paper Company saw an opportunity to drastically reduce the amount of pollutants released to the River and in July, 1990 implemented a Zero Discharge Program. The goal of this program is to eliminate all discharges of wastewater to the Mississippi River. This would eliminate all releases of conventional and toxic pollutants. In many industries, zero discharge is defined as a wastestream with concentrations of various substances below a technologically achievable detection limit, however, the wastestream still exists. Hennepin Paper Company's Zero Discharge seeks virtual elimination of the wastestream.

At the start of the Pollution Prevention Grant, the Zero Discharge Program had been going for approximately one year. This Pollution Prevention Grant was used to determine ways to allow continued reuse of wastewater, enhance wastewater quality for reuse, and eliminate toxicity of any water discharged to the River.

The papermaking process uses large volumes of water to produce a finished product. It is general practice in the paper industry to recycle certain wastestreams, however, large volumes of wastewater are still generated. Hennepin Paper Company operates its own activated sludge wastewater treatment plant to treat the wastewater from the paper mill. It is the papermaking process in general that produces the industrial wastewater at which this project is aimed.

To achieve the stated goals, existing technology was used in a new application. Much research has been completed on the reuse of municipal wastewaters, generally for irrigation. Hennepin Paper Company is not aware of any other integrated papermill that has attempted to completely recycle all wastewater.

PROCEDURES

The early stages of the project included collection of existing data on wastewater discharges before and after implementation of the Zero Discharge Program. This data helped determine flow patterns and provided information for pumping and piping changes.

The flow rates of many different wastestreams had to be measured in order for sound decisions to be made concerning zero discharge

system configuration. Since nearly all flows needing measurement were without flowmeters, two flow measurement devices were purchased. A strap-on transit time flowmeter was used to measure flow rates in pipes. This instrument was very useful in a number of difficult flow measurement areas. An open channel ultrasonic flowmeter was used in areas where flows could be contained in an open channel.

Several laboratory tests were conducted to analyze wastewater. Toxicity testing to determine wastewater lethality to the water flea *Ceriodaphnia dubia* were conducted. The exact procedures followed are documented in the laboratory reports contained in the appendices of this report.

Bench testing of various wastewater treatment technologies were performed and the resultant waters subjected to testing including toxicity testing.

TECHNICAL RESULTS

Before the Zero Discharge Program began, all of the mill's process and cooling water was supplied by the Mississippi River. Fresh water from the river entered the mill, passed over a fine mesh screen, entered a 2,700-gallon freshwater tank and was pumped by the house pump to process and cooling water demand points throughout the mill.

The resulting process wastewater was treated in the company-owned activated sludge wastewater treatment plant and discharged through a process wastewater outfall (outfall 01). The waste cooling water was discharged through a non-contact cooling water outfall (outfall 02). Figure 1 shows Hennepin Paper Company's wastewater treatment system before the closed loop system was installed.

Prior to the initiation of the Zero Discharge Program, a daily average of 607,000 gallons of process wastewater and 1.14 million gallons of cooling water were discharged to the river. By pumping increased amounts of treated wastewater into the freshwater tank using the closed-loop, system, the mill's process and cooling water is now nearly 100 percent recycled and the total volume of wastewater discharges to the river has fallen by 82 percent. Figure 2 shows the current configuration of the closed-loop recycling system.

The first steps taken in the Zero Discharge Program were to recycle the process wastewater back into the Freshwater tank. This was accomplished by placing a dam in the parshall flume that was used to measure the discharge rate and volume of outfall 01. This dam created a wet well (zero discharge sump) for three pumps termed zero discharge pumps. By placing the strap-on flowmeter on the pipe carrying wastewater to the wastewater treatment

plant, flow conditions through the zero discharge sump could be measured. Because of the dam in the parshall flume, and the zero discharge pumps extracting the water before it could be discharged, the open channel flowmeter that previously measured flow in the flume became useless. It was determined that two lift station pumps each had capacities of approximately 600 gallons per minute. The zero discharge pumps have a combined pumping capacity of 1290 gallons per minute.

Initially, river water entered the freshwater tank at an uncontrolled rate through an incoming water line. Occasionally, the water overflowed the tank and returned to the river. When the wastewater was routed to the freshwater tank, an automated valve was placed in the incoming river water line to prevent a mixture of river water and wastewater from overflowing to the river. The valve is controlled by a liquid level sensor in the freshwater tank. When the volume of water supplied to the freshwater tank is not sufficient to meet the demand of the house pump, the water level in the tank decreases, triggering the opening of the valve to allow river water to bring the level back up to the required amount. Once the water reaches a predetermined point, the automated valve closes. Conversely, when the supply of wastewater exceeds the amount required by the house pump, the wastewater overflows the tank and reenters the wastewater system.

Because the wastewater and river water were now being mixed and supplied as both process and cooling water, efforts began to eliminate the cooling water discharge. In March 1991, the entire cooling water flow was diverted to the Zero Discharge System. Figure 3 and Figure 4 illustrate the decline in volumes of process and cooling water 'respectively.

B y combining both process and cooling water systems into the closed-loop system, several problems arose. By assimilating all the cooling water into the loop, the flow of wastewater through the wastewater plant increased to a point where the plant became hydraulically overloaded, causing wastewater treatment efficiency to decline. This was partially caused by recycled wastewater that was delivered to the freshwater tank at volume levels that often exceeded what was required by the house pump. Treated wastewater would then overflow back into the wastewater treatment system' and be retreated, adding to the hydraulic load on the treatment system. In addition, the volume of process wastewater discharged through outfall 01 increased as can be seen on Figure 3 starting in April 1991.

To prevent the wastewater from overflowing, and existing above ground storage tank was converted into a surge tank. This tank was placed in between the number two zero discharge pump and the freshwater tank. The surge tank is at an elevation higher than

the freshwater tank, allowing the water pumped into the surge tank to be gravity fed to the freshwater tank. An automatic valve was placed in the pipe connecting the surge tank to the freshwater tank, and is operated by the same level sensor that operates the automatic valve controlling river water flow to the freshwater tank. The two valves work in concert to provide the necessary volume of water to the freshwater tank to satisfy the demands of the house pump. With this system, the surge tank valve opens first, and supplies recycled wastewater to the house pump. When the wastewater volume is insufficient, the river valve opens to meet the demand of the house pump, and then automatically closes when the wastewater from the surge tank can keep up with demand.

The surge tank initially had a capacity of approximately 50,000 gallons. Because the flow from the surge tank to the freshwater tank is gravity driven, there were times when the flow from the surge tank could not keep up with the demand of the house pump. As a result, river water would enter the freshwater tank to make up the shortfall. This situation was not desirable because there was sufficient wastewater to meet the house pump demand but it was a matter of delivery. To help overcome this problem, the surge tank volume was expanded.

The surge tank is a 38.5 foot diameter by 15 high cylindrical concrete stave tank. In order to increase capacity, leaks in the tank had to be eliminated. A plastic liner was installed in April 1993 which allowed surge capacity to increase to approximately 100,000 gallons. This additional capacity reduced the intake of river water by approximately 30,000 gallons per day.

The Zero Discharge Programs success in recycling wastewater created a problem -of biological growth in the mill's piping systems. In May, 1991, a chlorine dioxide generation system was installed to combat the microbial growth problems; Bacterial plate counts and subjective observations of maintenance problems due to biofouling showed that chlorine dioxide disinfection was successfully inhibiting excess growth. Heterotrophic plate counts give an estimation of aerobic bacteria that are present in the wastewater. These plate counts are only an indicator, of disinfection effectiveness. Subjective observations are generally more meaningful when evaluating disinfection results. Trials using' hydrogen peroxide as a replacement for chlorine dioxide were conducted with success (complete laboratory data on hydrogen peroxide disinfection trials is contained in Progress Report I located in Appendix 1). As a result of data collected in these trials, hydrogen peroxide has now replaced chlorine dioxide for disinfection purposes. The hydrogen peroxide is fed at 30 mg/l into the zero discharge 'sump. The residual concentration of peroxide in the wastewater system is monitored, weekly and if the residual in the treated wastewater reaches 25

mg/l, the feed is stopped until the residual is lowered to 5 mg/l.

One of the most difficult biofouling problems involved three shell and tube heat exchangers used to condense steam from the paper machine dryers for return to the boiler feedwater system, The recycled wastewater caused the cooling side of the tubes to become fouled, impeding heat transfer, causing a loss of steam and decreased production rates. City water was initially tried as an alternative to wastewater for this cooling application. However, city water is costly and added to the water burden on the recycling system. These problems were solved by installing a closed loop cooling water system for the heat exchangers. This system uses river water for make-up and is comprised of an induced draft counterflow cooling tower and a recirculation pump. Using the closed loop cooling water system has eliminated the use of approximately 100,000 gallons per day of city water that was previously used once and discharged to the wastewater treatment system, In addition, water purged from the closed loop cooling system to prevent solids build-up is now used in a crucial shower on the paper machine that cannot operate properly using recycled wastewater. By reusing this purged water, approximately 80,000 gallons per day of city water usage has been eliminated.

During the production of colored construction paper, the wastewater becomes colored from the dyes used to color the paper. One of the first problems was how to modify production using colored wastewater instead of clear river water. Originally, colored paper was manufactured on demand with no specific schedule for a particular color. With the use of colored wastewater, the manufacturing schedule. was arranged so the color of the wastewater would not affect the final color quality of the paper.

After experimenting with various formula combinations, it was found that a manufacturing schedule which started with lighter colors could progress to deeper and darker colors, culminating in black. After black, successively lighter shades could be made, such as grays, browns or blues, finally ending in white. This color manufacturing sequence has undergone several changes, a n d is continually adjusted based on timing of customer orders and amounts of each color manufactured. For instance, after black is manufactured, a sufficient amount of a dark colors must be made in order to be able to use the darker water before lighter shades can be made.

Several treatment technologies were tested to determine if a higher quality effluent could be produced which would ease some of the maintenance and manufacturing concerns inherent to wastewater recycling. Hennepin Paper Company's wastewater treatment plant does not have a primary clarifier, therefore,

significant amounts of wood fiber enter the aeration tanks for biological treatment. Bench testing of influent wastewater was completed to determine if primary clarification might have a positive impact on overall treatment. It was found that total suspended solids and biochemical oxygen demand could be reduced 59 and 17 percent respectively. Additional details can be found in Appendix 1, page 7 of Progress Report I.

Another issue this pollution prevention project dealt with was the toxicity of the wastewater. The treated wastewater was known to be acutely toxic to the water flea *Ceriodaphnia dubia*. Other organisms including *Daphnia magna* and the fathead minnow are also commonly used. *C. dubia* is used for toxicity testing due to its greater sensitivity to toxicants. Acute toxicity testing involves placing several of the test species in a test chamber containing 100 percent of the wastewater to be tested. In order for the wastewater to be deemed nontoxic, 50 percent of the organisms must be alive after 48 hours. If greater than 50 percent are dead at the end of this time period, the water is considered acutely toxic.

In the past several studies (not part of this project) were conducted to try to determine the source of toxicity in the wastewater. Normally, samples of water can be taken at each step in the paper manufacturing process and tested to see where toxicity is introduced. However, by recycling the wastewater the water entering each step is already toxic making it impossible to determine the source. As part of this project, a Mill Simulation and Toxicity Test was performed by Integrated Paper Services. This simulation took all raw materials from Hennepin Paper Company's manufacturing process and duplicated the papermaking process in a laboratory, taking samples of water after each step as described above. It was determined that each step in the process produced water with some degree of toxicity. It was determined that toxicity increased the most after the addition of the dyes. In the papermaking process, the final mixture of water, fiber and dyes is placed uniformly on a wire on the paper machine. The wire is actually a continuous belt made of nylon mesh. This wire holds the fiber to form a continuous sheet of paper while the water drains through the wire and becomes whitewater; This whitewater, which contains residual dye, is then recycled back to the fiber preparation area for reuse. In the mill simulation the whitewater was recycled ten times. There was some question as to whether or not defoamer added to the whitewater could be the main cause of toxicity. However, toxicity reached its peak after five cycles. If defoamer were the toxic agent, toxicity would continually increase because defoamer is continually added to the whitewater. Complete procedures and results of this Mill Simulation are included in Attachment 5 of Progress Report II which is attached as Appendix 2 of this document.

Several treatment methods were investigated to determine if toxicity of the wastewater could be eliminated. Wastewater samples were dosed with either 2 mg/l or 25 mg/l chlorine dioxide or 20 mg/l or 100 mg/l hydrogen peroxide to determine if the toxic agent could be eliminated by oxidation. Toxicity testing of the treated water showed no decrease in toxicity. See Appendix 3.

Powdered activated carbon was used to treat samples of wastewater to determine if carbon adsorption could remove toxicity. It was found that powdered activated carbon when mixed with the wastewater sample and filtered out, eliminated the toxicity. This procedure was completed twice by Integrated Paper Services (see Appendix 3 and Mill Simulation results in Appendix 2) and once by Hennepin Paper Company with toxicity testing done by Environmental Monitoring' Incorporated (see Appendix 2, Attachment 6). In addition to powdered activated carbon, granular activated carbon in a filter was tested. In all activated carbon tests, color in the wastewater was 100 percent removed. The granular activated carbon filter produced a nontoxic wastewater also (see Appendix 2, Attachment 7).

Some areas of the papermaking process require water of higher quality than the recycled wastewater. For these applications, city water or river water must be used. Because these sources of water are continually added to the closed loop system, the surge tank would occasionally overflow back into the wastewater system. The open channel flowmeter that was purchased was set up in a weir box to measure the volume of water that would overflow the surge tank. It was found that an average of 300,000 gallons per day would overflow the surge tank. At the same time, an average of 40,000 gallons of water was being discharged to the river because the zero discharge pumps could not keep up with the water overflowing the surge tank. This showed that the excess, 260,000 gallons per day of treated wastewater was returning needlessly to the wastewater treatment plant. Again, this water only added to the hydraulic load to the wastewater plant.

At this point a temporary pipe was installed that routed the water that overflowed the surge tank to the 01 outfall. The discharge to the river did not increase, however, the hydraulic load on the wastewater treatment plant decreased. At this point it was realized that the excess of approximately 40,000 gallons per day would have to be treated and rendered nontoxic before it could be discharged to the river.

In order to achieve this goal, a wastewater polishing system was installed to treat the excess 40,000 gallons per day. The polishing system consists of a sand filter and an activated carbon filter which will draw water from the surge tank. The sand filter will remove suspended solids from a continuous

slipstream of 120 gallons per minute and return the water to the freshwater tank. When excess water begins to accumulate in the surge tank, a level sensor will start a pump which will route 80 gallons per minute of sand filter discharge through the activated carbon filter. This filter will remove the color and dissolved organics in the wastewater. This polished water will then be routed initially to the closed loop cooling water system to replace river water make-up. Together these filters will remove the suspended solids and color in the wastewater so it will be of high enough quality to replace several river water or city water usage points within the papermill. By replacing these sources of water from outside the closed loop, all wastewater should be completely recycled achieving the goal of zero discharge. Appendix 4 contains the process control description, hydraulic schematic diagram of the polishing system, and product sheets for the sand filter and carbon filter.

Currently this *polishing system is in the shakedown phase. The system operation to date has been very good. Some reprogramming of the control system is necessary before the entire system can function automatically which will allow maximum reuse of the polished water.

Wastewater polished through the system has been tested and found to be nontoxic. Appendix 5 contains the laboratory results of this test.

POLLUTION PREVENTION ACHIEVED

With this configuration, the total volume of industrial wastewater discharged to the Mississippi River after the inception of the Zero Discharge Program has decreased by more than 82% (Figure 5). A comparison of a typical month before Zero Discharge to a typical month after, shows a 98% reduction in discharge (Figure 6).

By drastically reducing the volume of wastewater discharged to the river, the mass of conventional pollutants released to the environment is also greatly reduced. Comparing the twenty nine months before and after the initiation of the Zero Discharge Program shows reductions of 51% and 79% for biochemical oxygen demand (BOD) and total suspended solids (TSS) respectively. This data is illustrated in Figure 7.

This decrease in discharge also translates into reduction in release of wastewater which has been shown to be toxic to water fleas. In addition, basic green 4, a component of a green dye used in the papermaking process is a toxic chemical according to Section 313 of the Emergency Planning and Community Right-to-Know Act. The Zero Discharge Program has reduced the release of basic green 4 by 81 percent.

The main components of the Zero Discharge System are the zero discharge pumps, surge tank, sand filter, and carbon filter. To date the only maintenance problems have been with the pumps. The pumps used are vertical centrifugal pumps which are designed for use in sealed sumps. The zero discharge is open and occasionally the level in the sump rises to a point where pump bearings not designed to get wet become submerged. This necessitates the replacement of the bearings. Recent work which raised the pump in the sump appears to have solved the problem.

The sand filter is designed to continuously wash the sand during operation so no downtime is required for backwash. The sand filter has been operational for approximately two months and no major operational or maintenance problems have been encountered.

The carbon filter has only been operated for 10 days. Backwash is required approximately every third day. Backwash time is generally thirty minutes. In the 10 days the filter was operated, in excess of one million gallons of water was treated. The carbon then became spent and color began breaking through. Replacement of the spent carbon is expected to take approximately four hours.

The treatment technologies investigated in this project were implemented as rapidly as possible. Although this project has been extended longer than originally anticipated, the installation of the filtration system was completed as rapidly as possible in order to have it be included in this report.

By recycling wastewater, the pollutants do not get a chance to be released-to the environment, but instead are given another chance to become part of the product that produced them initially. The only transfer of pollutants that could occur as a result-of the Zero Discharge Program would be from water to air as a result of thermal regeneration of activated carbon; Regeneration of the carbon will be completed by the vendor, Calgon Carbon Corporation.

ECONOMIC ANALYSIS

The total cost to implement the technology studied in this project includes costs for disinfectant chemicals, surge tank lining, and filter system purchase and installation.

The cost of using chlorine dioxide as a disinfectant averaged approximately \$288 per day. This cost includes chlorine gas, sodium chlorite, and city water. Currently, hydrogen peroxide disinfection costs \$105 per day for a feed rate of 30 mg/l.

Lining the surge tank was an integral part of completing the filtration system. Original plans called for the demolition of the concrete stave tank and replacing it with a bolt-together

steel tank. The total cost would have been in excess of \$40,000. Instead, the concrete tank was lined with plastic and the entire project cost was \$22,000.

The filter system includes a sand filter, activated carbon filter, electrical controls, and associated pumps and piping. Through March, the total amount spent on this system was \$223,431. There are few miscellaneous charges not processed at the time of this writing. Total project cost is expected to be \$240,000.

Implementation of the Zero Discharge Program and the filter system did not save Hennepin Paper Company money. Factors such as an improved public image and reduced public pressure, liabilities and regulatory problems are benefits that are less quantifiable than most pollution prevention projects. Most pollution prevention projects involve substituting raw materials which yield cost and pollution prevention benefits which are easily quantifiable. Hennepin Paper Company's 'Zero Discharge Program attempts to do as much environmental benefit as is possible by eliminating releases of industrial wastewater to the Mississippi River. Because of the benefits of less tangible factors, Hennepin Paper Company was willing to bear the expense of achieving pollution prevention through its Zero Discharge Program.

No other method to achieve zero discharge in the paper industry is known. Some state of the art pulp mills use evaporators to eliminate discharge to surface waters, however the pollutants are simply transferred to the air or land.

There are several alternatives to activated carbon filtration. Chemical oxidation proved to be ineffective at removing color in the wastewater. Ozone was investigated, however, due to the high capital costs to implement (in excess of one million dollars), its use was not considered.

CONCLUSIONS

The environmental benefits of this project are drastically reduced discharges of industrial wastewater and associated pollutants. This reduction in discharge may allow the company to be classified as a minor wastewater discharger. This would be beneficial in that reporting requirements may be relaxed. As stated previously, economic benefits are not calculable.

A total wastewater recycling system may be feasible at other papermills of industry which do not require exceedingly high process water quality. The closed loop cooling water system is definitely applicable to a variety of users. The filter system to polish an excess of wastewater for use in a cleaner application also holds promise of other applications. The key in

all of these applications is to reexamine water usage points and water wasting points and determine if there might be a point where the waste could be compatible with the usage point. Even if it may -take increased treatment or rearrangement of a manufacturing sequence, the potential is worth exploring.

RECOMMENDATIONS

The first step in a program such as the Zero Discharge Program would be to do a detailed water balance. In this case the program was started with very little study into the water balance and problems were dealt with as they arose. As stated above, it must be determined if wastewater is of high enough quality for reuse. The impact that a recycling process will have on the quality of the wastewater will also have to be addressed.

Corporate management must be environmentally progressive in order to embark on a novel pollution prevention project. Many times minimal compliance becomes the goal. Hennepin Paper Company's management was entirely committed to the goals of the Zero Discharge Program.

Hennepin Paper Company has National Pollutant Discharge Elimination System (NPDES) permit which allows discharge to the Mississippi River. The recycle system will have an impact on how future permits will be written. No special permits were necessary for implementation of the system, however, close communication has been maintained with the Minnesota Pollution Control Agency throughout the program.

The largest barrier to pollution prevention is economic. With increasingly stringent standards being imposed, greater amounts of money are being spent for general compliance and programs such as the Zero Discharge Program may never be able to be funded.

Paper manufacturing requires large volumes of water so most mill are located in areas where an un-interruptable supply and a stream for discharge are nearby. This creates the situation where as long as compliance is maintained, discharging wastewater is the most 'economical way to deal with the wastestream. In areas where this is the case, implementing a program like the Zero Discharge Program requires 'much determination and self motivation on the part of the company to strive for any further environmental controls.

BUDGET SHEET

	Total \$	State \$	Matching \$
Labor	21,170.14	16,169.74	5,000.40
Materials	234,589.80	1,028.97	233,560.83
Testing	5,827.00	5,827.00	0
Misc.	6,974.29	6,974.29	0
	268,561.23	30,000.00	238,561.23

FIGURE 1. OLD WASTEWATER TREATMENT SYSTEM

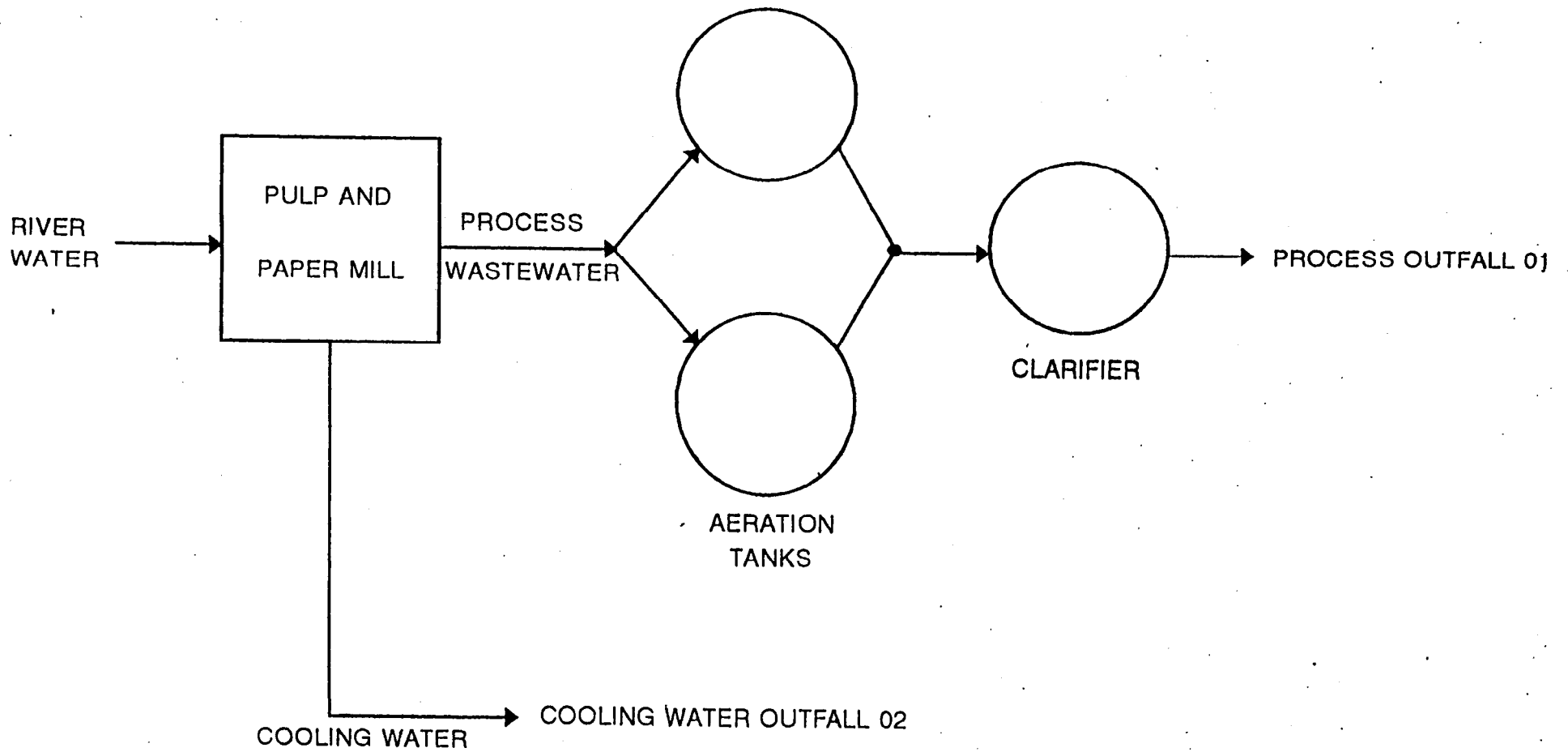


FIGURE 2. CLOSED LOOP WASTEWATER RECYCLING SYSTEM

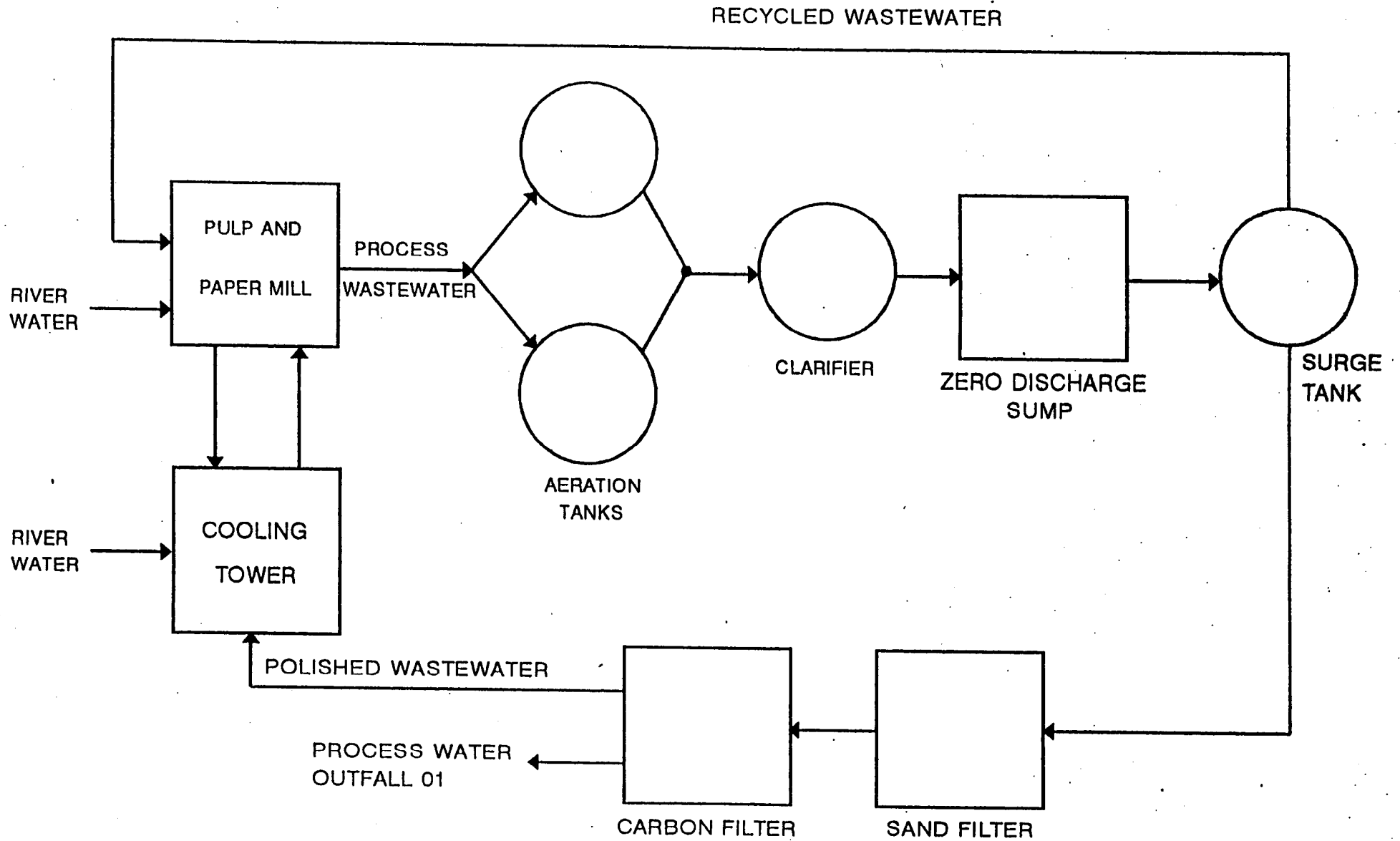


FIGURE 3

PROCESS WATER DISCHARGE, OUTFALL 01

JAN 1990-APR 1991 MONTHLY AVERAGES

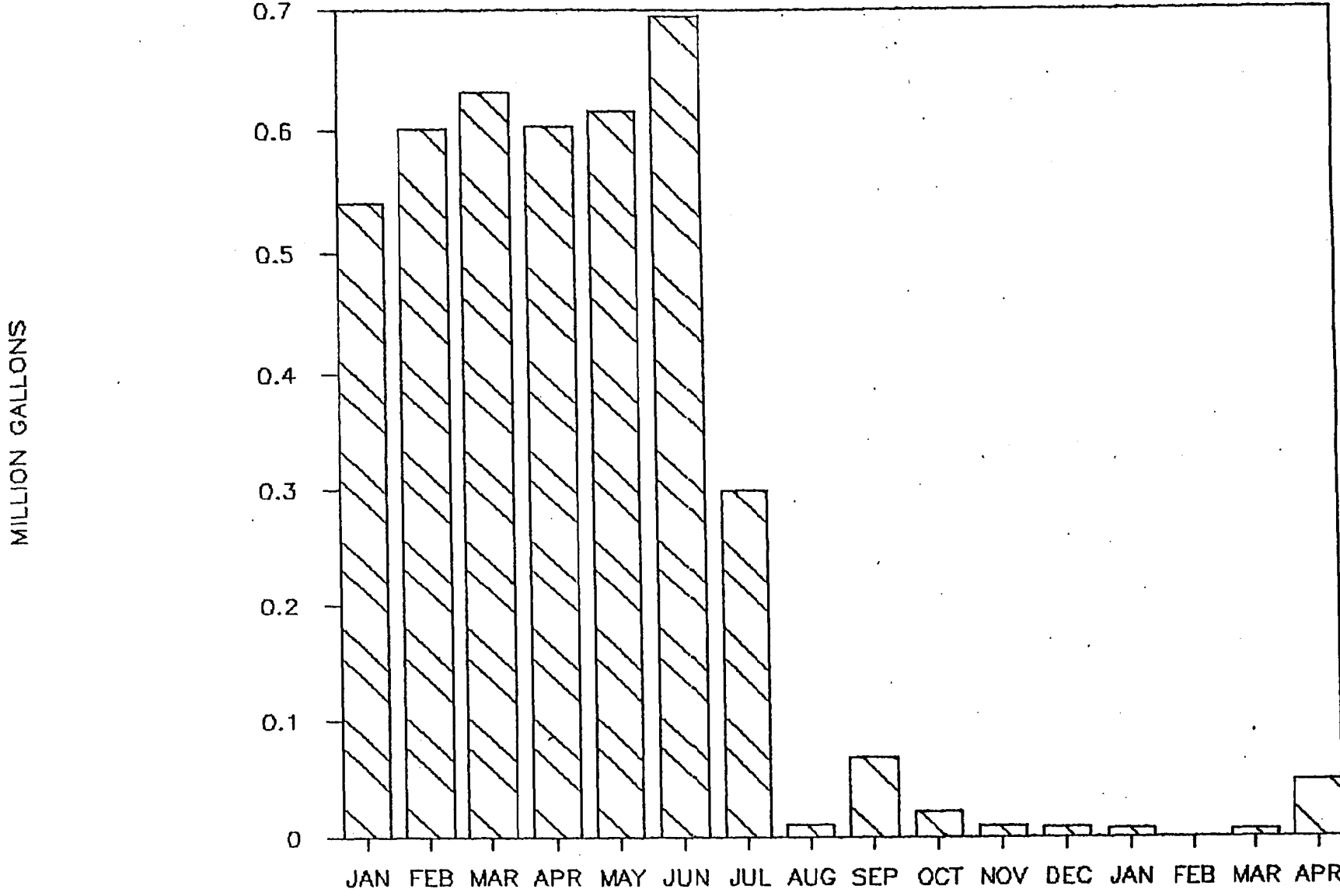


FIGURE 4

COOLING WATER DISCHARGE, OUTFALL 02

JAN 1990-APR 1991 MONTHLY AVERAGES

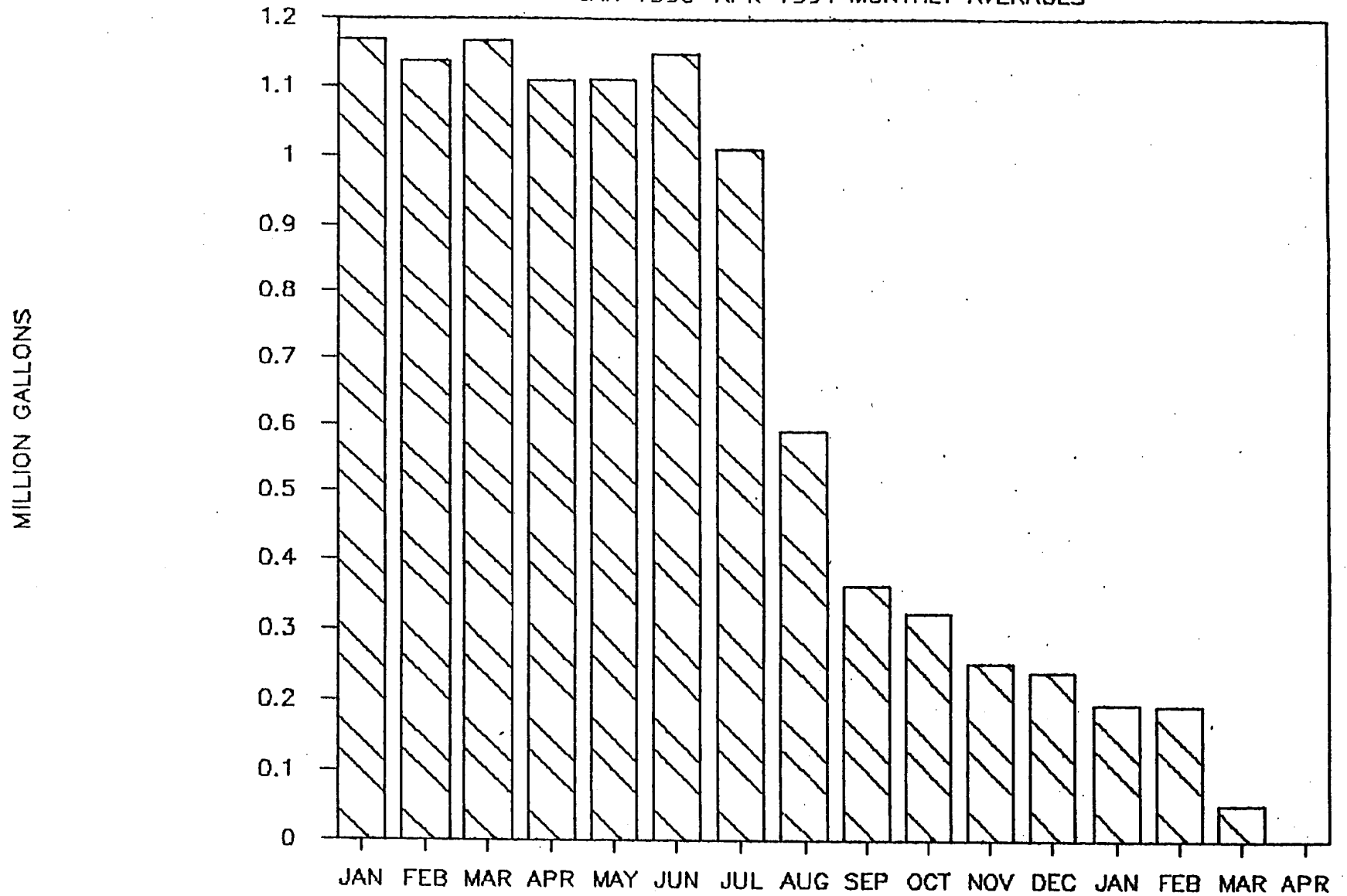


FIGURE 5

WASTEWATER DISCHARGES

REDUCTIONS FROM ZERO DISCHARGE PROGRAM

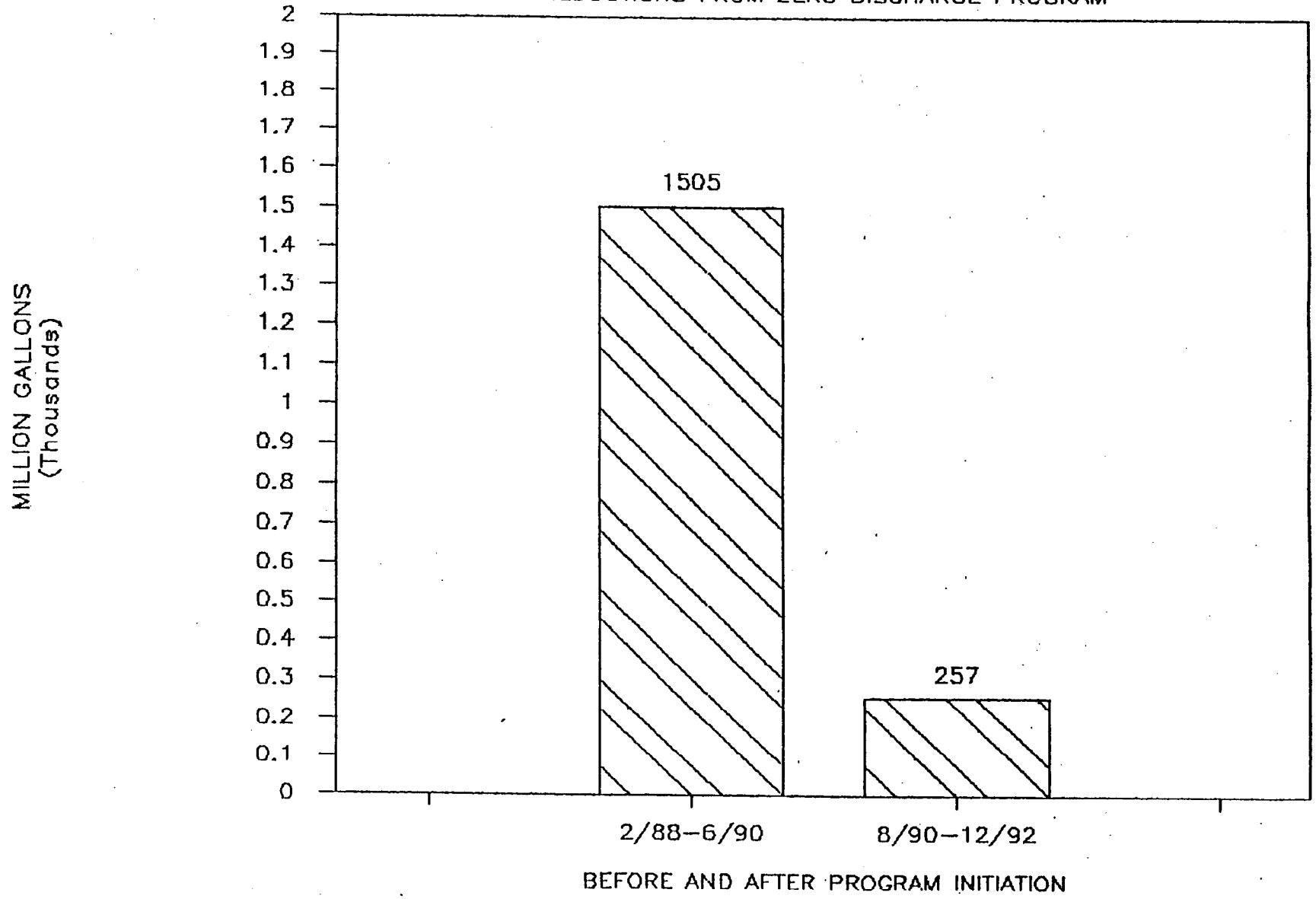


FIGURE 6

WASTEWATER DISCHARGES

REDUCTIONS FROM ZERO DISCHARGE PROGRAM

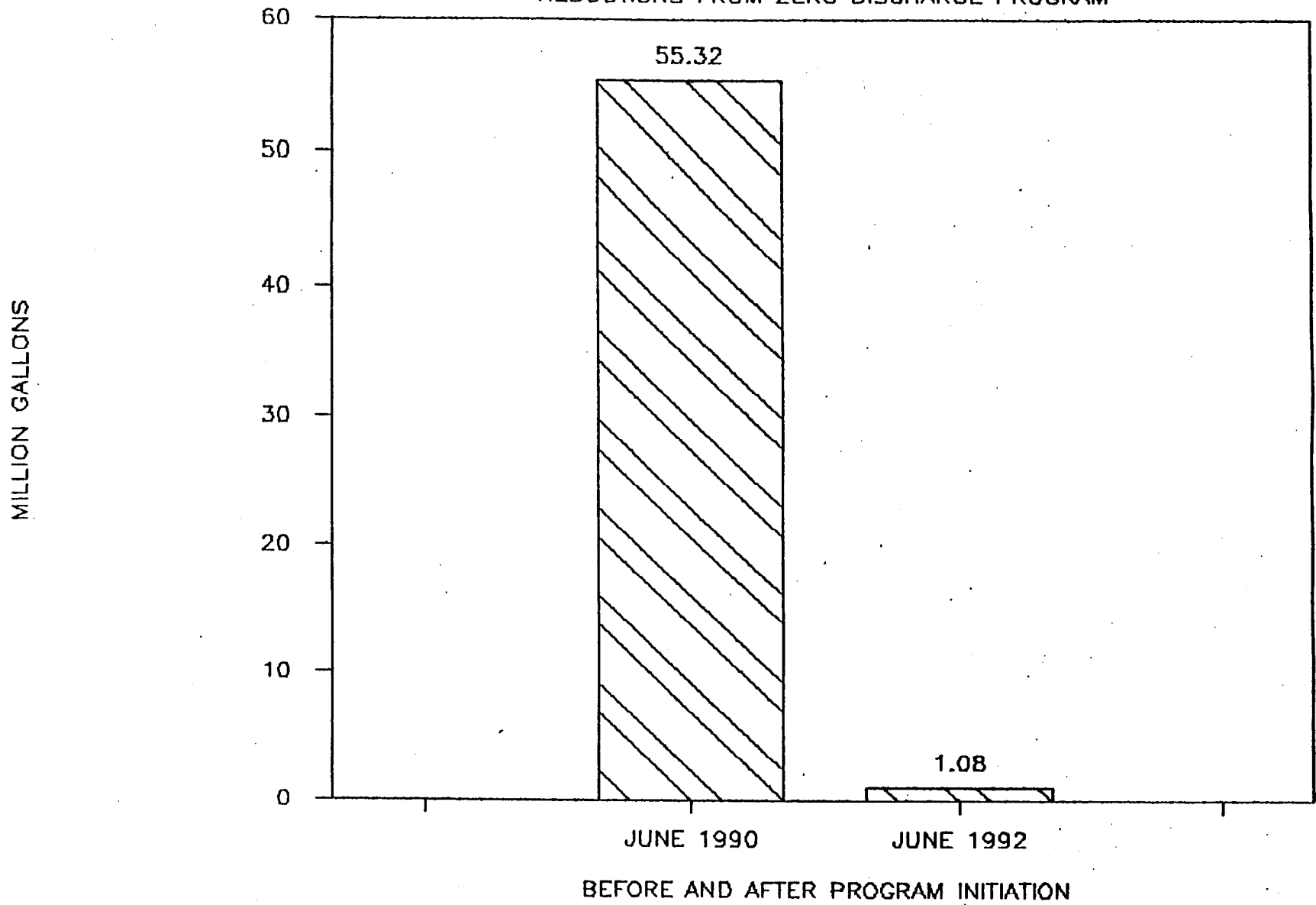
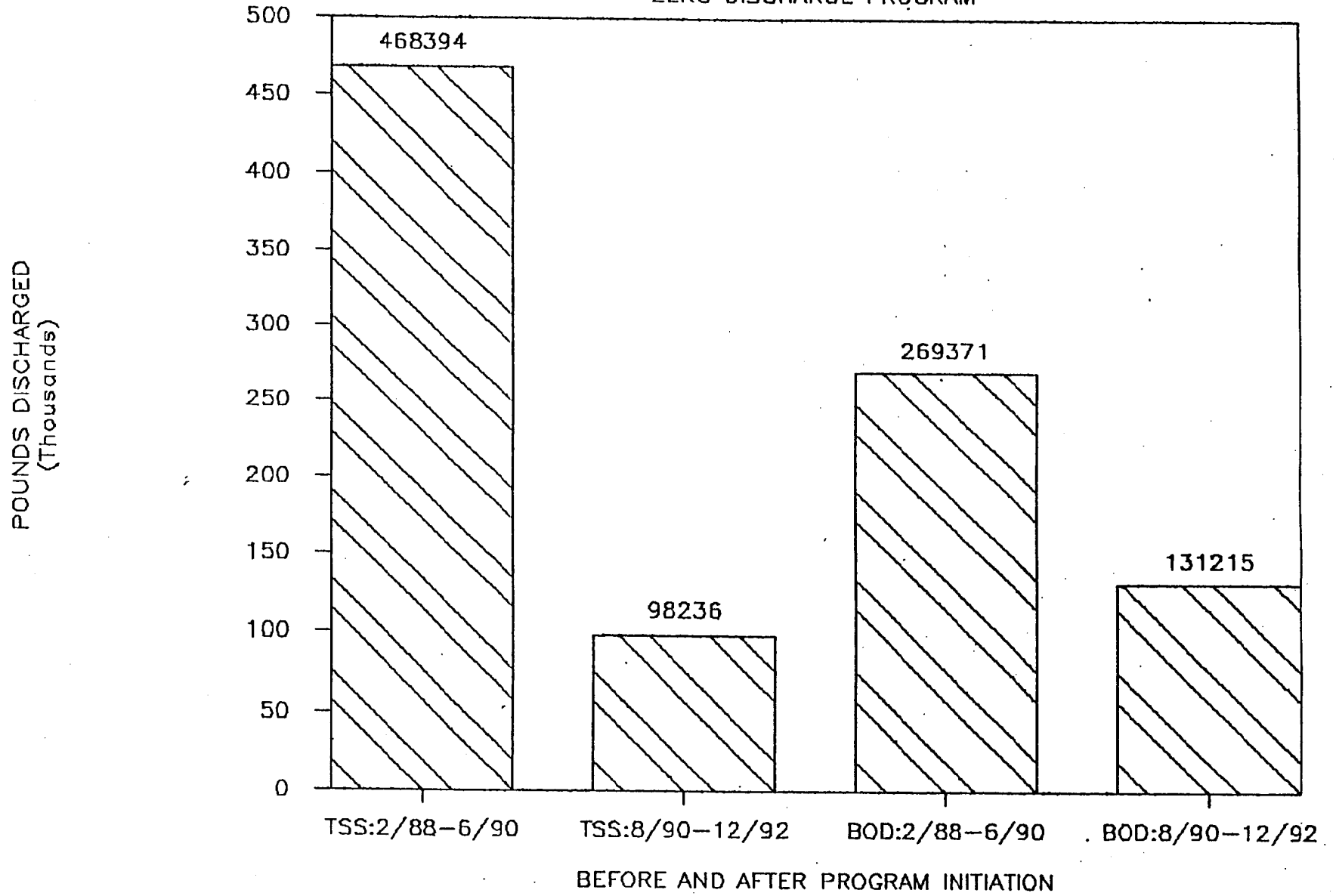


FIGURE 7

POLLUTION PREVENTION, TSS and BOD

ZERO DISCHARGE PROGRAM



Components Required for Study.

I T E M	AMOUNT NEEDED
Poplar	30 lb. bolt (or end cuts)
Kraft Pulp'	2 lb. OD Basis
Secondary Fiber	2 lb. OD Basis
Nalco Microbiocide	5 g
Nalco Dispersant	20 g
Dumar Defoamer	20 g
Color	50 g
Alum	100 g
Ogilvie Cato-Starch	25 g
Henkel Foamaster	5 g
Bleach Liquor	500 mL

TIMETABLE

This project can be started within two weeks of acceptance of this proposal. The final report will be delivered within 15 working days after completion of the laboratory work.

STAFF

Process simulation will occur in the pulping and bleaching laboratory; toxicity testing will occur in the aquatic toxicology laboratory. The primary contact for this project will be George Buttke. Questions regarding process simulation can be directed to Tom Paulson.

determine which part(s) of the process contributes most to the toxicity observed in the system. A list of components to be furnished and a list of operational parameters to be completed by Hennepin are attached.

To duplicate (as best possible) the mill process, IPS will start with groundwood preparation using wood supplied by Hennepin. The wood will be "pulped" using a Sprout-Waldron 10" single disk refiner at a consistency of 1.5%. This prepared groundwood will be combined with kraft pulp and secondary fiber in a 50:20:30 ratio (mill supplied). This mixture will be bleached according to mill procedures, using mill supplied chemicals. Samples for toxicity testing will be taken after groundwood preparation and repulping of the kraft/secondary fiber mixture, and bleaching.

The bleached stock will be beaten to a predetermined freeness level. During beating, color will be added (weighted mixture of five most used dyes) and alum will be added. After color and alum additions, samples will be taken for toxicity tests.

For machine simulation, handsheets will be formed in a Buchner funnel, with the resultant "whitewater" recycled to simulate buildup. To determine the effect of solids buildup to equilibrium, samples will be taken for toxicity tests after one, five, and ten passes through the Buchner funnel. Mill defoamer will be added at the specified usage rate.

TOXICITY TESTING

This experimental plan will generate a total of ten samples for toxicity testing. Time-to-lethality tests will be used to assess the toxicity of these samples to the cladoceran *Ceriodaphnia dubia*. The goal of test interpretation will be to identify the point of greatest toxicity addition.. This process is not possible with the current recycling of treated wastewater into the 'mill.

BUDGET

The cost estimate for this project is \$2950.00. A breakdown for this estimate is listed below.

Process Simulation	\$1750
Toxicity Testing	\$ 900
Reporting	\$ 350

Hennepin Paper Company mill process simulation and sampling points for toxicity testing.

Initial Groundwood Preparation	Toxicity Test
Biocide, Dispersant, and Defoamer Addition	Toxicity Test,
Repulping of Secondary Fiber and Kraft Pulp	Toxicity Test
Bleaching of Mixed Stock	Toxicity Test
Pulp Beating (Valley Beater)	
Color Addition	Toxicity Test
Alum Addition	Toxicity Test
Retention Aid(s) Addition	Toxicity Test
Papermaking (Buchner Funnel)	
First Pass	Toxicity Test
Five Passes	Toxicity Test
Ten Passes	Toxicity Test

Proposal No. 39
Version 2

Simulation of Hennepin Paper Company's Mill Process Elements and
Toxicity Assessment of Resulting Process Waters

OBJECTIVES

Objectives of the proposed study are to (a) identify the cause(s) of toxicity in Hennepin Paper's mill wastewater, and (b) recommend possible solutions to the toxicity problem. Samples for analysis will be obtained through laboratory simulation of the papermaking process.

INTRODUCTION

Hennepin Paper is a specialty mill, producing primarily colored construction grade paper. The furnish used in the papermaking process is a mixture of mill produced groundwood and purchased Virgin and secondary fiber.

Currently, process wastewaters are sent to the mill's wastewater treatment system, and treated water is recycled into the mill for use as make-up water. Previously, only a portion of the treated wastewater was recycled into the mill, with the majority being discharged to the receiving stream. Repeated toxicity testing of treated wastewater, before and after the recycle program was initiated, indicated significant and persistent acute toxicity.

Work was initiated at IPS to determine the cause of effluent toxicity. The plan was to obtain samples from each process stream and determine toxicity. Before this plan could be implemented, the mill started recycling 100% of the treated effluent back into the process.. This made it difficult to precisely determine which process stream or streams were responsible for the toxicity.

This proposed project will try to identify which stream or streams contribute to the toxicity by simulating the mill's process in the laboratory (starting, with "clean" process water). This will be accomplished by using furnish and additives supplied by the mill. "Process" water will be local river water shown to be non-toxic. Volume requirements preclude the use of the receiving stream in the experiment. A schematic of the mill simulation process is given in the experimental plan.

EXPERIMENTAL PLAN

IPS will simulate the mill process in the laboratory, starting from groundwood preparation through the paper machine, to



March 23, 1992
Proposal Number 39
Version 2

Mr. Ron Klinker
Hennepin Paper Company
P.O. Box 90
Little Falls, Minnesota 56345

Dear Ron:

Enclosed please find the final copy of the proposal for the mill simulation and subsequent toxicity tests. I believe the program we have developed will provide the information needed to understand the source(s) of toxicity in the mill.

For formal approval of the proposal, please complete the bottom portion this letter (duplicate enclosed), and return it to IPS.

Thank you.

Sincerely,

George Buttke
Biologist
Environmental Bioassessment

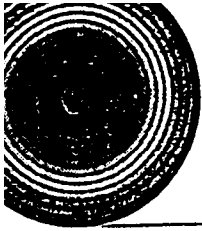
Enclosures

ACCEPTED AND APPROVED

Hennepin Paper Company

Proposal No. 39
Version 2.

By Ron Klinker Date 3/25/92
Purchase Order No. _____ No. of reports 3
To be sent to Ron Klinker



Hennepin Paper Company

P.O. Box 90, Little Falls, MN 56345 • (612) 632-3684 • 1-800-328-8520 • Fax 612-632-2574

February 25, 1992

Mr. George Buttke
Integrated Paper Services, Inc.
P.O. Box 446
Appleton, Wisconsin 54912-0446

Dear George,

What follows is an explanation of our bleaching process.

Our bleach liquor is batch mixed in the following volumetric proportions:

Water	90.5%
Sodium Silicate (35-40%)	3.1%
Sodium Hydroxide (50%)	3.1%
Hydrogen Peroxide (50%)	3.3%

The stock to be bleached (secondary fiber, groundwood) is adjusted to a pH of 8.0 with sodium hydroxide prior to bleach liquor addition. Bleach liquor is added at 0.12 gallons per pound of dry fiber. The temperature of the bleached stock is between 110-120) degrees Fahrenheit. The holding time in the bleach tank is between 1 to 1-1/2 hours. The bleached stock is then neutralized with sulfur dioxide to a pH of 6-7.

George, if you need more detailed information, please let me know.

Sincerely,

Ron Klinker
Environmental Affairs Manager

de

Page 2

Mr. George Buttke

February 7, 1992

toxicity. I have also included a copy of the M.S.D.S. for all of the chemicals' listed. With successful completion of this project, we anticipate discovery of the cause of toxicity, and with this information it is hoped we can eliminate or treat that cause.

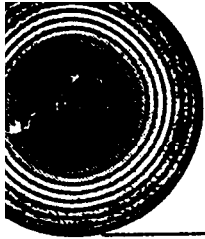
We would like to proceed with this project as soon as possible. If you have any questions, please let me know. I look forward to your updated proposal.

Sincerely,



Ron Klinker
Environmental Affairs Manager

de



Hennepin Paper Company

P.O. Box 90, Little Falls, MN 56345 • (612) 632-3684 • 1-800-328-8520 • Fax 612-632-2574

February 7, 1992

Mr. George Buttke
Integrated Paper Services, Inc.
P.O. Box 446
Appleton, Wisconsin 54912-0446

Dear George,

Here are the raw materials and chemicals used in our paper making process, and their feed rates.

Our average furnish mixture is:

Groundwood (Poplar):	50%
Purchased Kraft:	20%
Secondary Fiber:	30%

In the Pulpmill, the following chemicals are added to the white water:

Nalco Nalcon 7620-WB Microbiocide:	0.096 grams per pound of groundwood (dry)
Nalco 7613 Dispersant:	0.461 grams per pound of groundwood (dry)
Dumar DM-40-AD4 Defoamer:	0.491 grams per pound of groundwood (dry)

Once the three furnish sources are combined, the following chemicals are added to the beater in the listed order:

Color:	7.30 grams per pound of furnish (dry)
Alum:	31.68 grams per pound of furnish (dry)

For color, a mixture of our five most used dyes will be provided. The percentage of each dye in the mixture is weighted according to its actual use.

After the beater is dropped to the machine chest, an internal starch is added on some grades. When added, the feed rate is:

Ogilvie Cato 15 Starch:	4.99 grams per pound of furnish (dry)
-------------------------	---------------------------------------

A defoamer is added to the paper machine white water system

Henkel Foamaster DF-212:	0.797 grams per pound of furnish (dry)
--------------------------	--

George, these are the chemicals that are added in the paper making process which may pass through to the waste water system and cause

ATTACHMENT 1

The waste water sample passed through the GAC filter also showed decreased toxicity. Complete mortality of the C. dubia specimens was reached in three hours. The GAC treated sample showed no acute toxic effects at 48 hours, at which point the test was terminated. Detailed results are contained in Attachment 7.

EXPENDITURES

For Tasks 4 and 5, \$11,641.74 has been expended. The costs breakdown is as follows:

	<u>TOTAL \$</u>	<u>STATE FUNDS \$</u>	<u>MATCHING FUNDS \$</u>
Labor	\$ 1,608.90	\$ 1,608.90	\$.00
Materials	1,028.97	1,028.97	.00
Testing	3,750.00	3,750.00	.00
Misc.	5,253.87	1,287.21	3,966.66
	<u>\$11,641.74</u>	<u>\$ 7,675.08</u>	<u>\$ 3,966.66</u>

Invoices available at the time of writing are included as Attachment 8: The following is a total cost breakdown for this Pollution Prevention Project:

	<u>TOTAL \$</u>	<u>STATE FUNDS \$</u>	<u>MATCHING FUNDS \$</u>
Labor	\$ 4,982.40	\$ 4,982.40	\$.00
Materials	5,305.97	1,028.97	4,277.00
Testing	4,062.00	4,062.00	.00
Misc.	5,893.29	1,926.63	3,966.66
	<u>\$20,245.66</u>	<u>\$12,000.00</u>	<u>\$ 8,243.66</u>

This breakdown shows that costs for this project have been funded 60% by State grant money, and 40% matching funds from Hennepin Paper Company.

PAC is usually applied to waste water in a single dose and after a given contact time is removed through sedimentation or filtration. GAC is normally utilized in filtration columns. Bench scale testing used both PAC and GAC methodologies. Attachment 2 details the procedures for the testing.

Work completed as part of Task 2 showed that removal of wood fibers from waste water influent could enhance the efficiency of the Waste Water Treatment Plant, allowing for higher quality recycled water. Investigation into numerous filtration devices led to a decision to pursue some type of static screen for waste water filtration. Side hill wedge wire screens are commonly used in the paper industry for the fiber recovery in paper machine white water loops. A side hill screen uses the action of water traveling over a screen to separate solids from liquid. This type of screen is attractive in that it has no moving parts, and it's relatively low capital cost. Attachment 3 gives an overview of this type of screen. There are numerous manufacturers of this type of screen. Ron Klinker and Al Loken of Hennepin Paper Company traveled to Globe Manufacturing in Cornell, Wisconsin to view four previously-used Bauer Hydrasieve screens and talk to the Plant Engineer about the screens performance. Hennepin Paper Company has made a bid on these used screens and is awaiting a reply from Globe Manufacturing.

To determine the feasibility and best placement of this type of screening device, Delta Environmental Consultants, Inc. were contracted to inspect the project area and design the best piping route. Delta helped designate a feasible location for a filter system and made drawings of the best route. These drawings only show the route and allow for various filtration systems to be inserted. The results of Delta's work are found in Attachment 4.

RESULTS

Mill simulation toxicity testing showed that all components used in the paper making process yielded some degree of toxicity. This study indicates a strong relationship between dyes and toxicity. This follows the fact that color removal via activated carbon also removes toxicity. However, several other organic compounds and metals may be removed by activated carbon. Complete mill simulation results are found in the report by I.P.S., which is included as Attachment 5.

Toxicity testing of the waste water sample treated with PAC showed decreased toxicity. Complete mortality in the straight effluent was reached in approximately 4.5 hours, while complete mortality was not reached until 44 hours in the PAC treated sample. Detailed results are contained in Attachment 6.

INTRODUCTION

Hennepin Paper Company manufactures primarily colored Construction Paper at a paper mill in Little Falls, Minnesota. The mill is located on the west bank of the Mississippi River, and has been in operation since 1890. In July, 1990, Hennepin Paper Company initiated a Pollution Prevention Program termed Zero Discharge. The goal of this program is to eliminate all discharges of waste water to the Mississippi River by recycling that water back into the manufacturing process.

The fourth task of this project is aimed at the identification and possible elimination of the source or sources of toxicity in the recycled waste water. A bench scale mill simulation study and bench scale treatment testing provide information on toxicity reduction. by recycling the process waste water, only a small portion of fresh river water is introduced to the system and conversely, only a small amount of waste water is discharged to the River. This examination of toxicity is important because recycling does not allow for purging or dilution of the toxic agent, but instead an increased concentration throughout the system. The information necessary for the elimination of this toxicity in the small volumes of waste water that are discharged was the data collected in Task 4.

PROJECT STATUS AND PROCEDURES

This portion of the project involved a bench scale simulation project entitled "Simulation of Hennepin Paper Company's Mill Process Elements and Toxicity Assessment of Resulting Process Waters." This work was performed by Integrated Paper Services (I.P.S.) in Appleton, Wisconsin. Explanation of raw materials usage was sent to I.P.S. by Hennepin Paper Company in order to determine the most appropriate methodology and feed rates. This information was used to generate the proposal for the simulation project. All of this information is included in this report as Attachment 1. The procedures followed will not be restated in this text as explanation is given in Attachment 1.

Concurrent with mill simulation testing, bench scale testing of treatment technologies to remove toxicity were performed. Previous work conducted as part of Task 2 has shown that oxidation is not a viable, treatment technology for toxicity reduction. Task 4 work concentrated on absorptive treatment technologies.

Activated carbon is well known for its ability to absorb a variety of contaminants from water. The waste water at Hennepin Paper Company is normally colored as a result of dyes used in the manufacturing process. Treatment with activated carbon was tested to determine color removal capabilities and toxicity reduction potential. Activated carbon is used in two forms, powdered activated carbon (PAC), and granular activated carbon (GAC). PAC is usually derived from wood or peat, and GAC normally originates from coal.

ZERO DISCHARGE PROGRAM
AT AN UNCOATED GROUNDWOOD PAPER MILL

PROGRESS REPORT II

BY

Ronald T. Klinker
Environmental Affairs Manager
Hennepin Paper Company
100 Southwest Fifth Avenue
Little Falls, Minnesota 56345

This project is funded through a Pollution Prevent Grant from:

The Minnesota Office of Waste Management
1350 Energy Lane
Saint Paul, Minnesota 55108

Grant Program Contact:

Julie MacKenzie, Coordinator
Pollution Prevention Grant Program
Minnesota Office of Waste Management
(612) 649-5494
MN Toll Free: 1-800-652-9747

APPENDIX 2

TABLE 4 (continued)

11/19/91	9000000	150000	
11/21/91	900000		
11/23/91	2000000	980000	HYDROGEN PEROXIDE STOP
11/26/91	200000	160000	

TABLE 4

HENNEPIN PAPER COMPANY - ZERO DISCHARGE PROGRAM
 HETEROTROPHIC BACTERIAL PLATE COUNTS
 COLONIES PER 1ML

DATE	SAMPLE LOCATION		
	ZERO DISCHARGE SUMP	MILL HOSE	
2/12/91			1000
2/14/91			137000
2/20/91			29000
3/5/91			8000
3/15/91			10400
4/16/91			1000000
5/1/91			3700000
5/9/91			190000
5/9/91/	540000		
5/10/91	850		
5/15/91			168000
5/16/91	65000		
5/17/91	44000		
5/23/91	220000		
6/6/91			140000
6/7/91	61000		
6/14/91	220000		280000
6/19/91	450000		
6/21/91	1220000		
6/26/91	1800000		
6/28/91	140000		
7/1/91	1770000		1500000
7/3/91			3000000
7/10/91			2500000
7/17/91			310000
7/17/91	5600000		
8/2/91			2100000
8/13/91			4500000
8/26/91	700000		9600000
8/30/91			122000
9/4/91			10000000
9/13/91			2200000
9/16/91	3400000		2800000
9/25/91	3600000		3100000
9/26/91	160000		250000
9/26/91	5900000		6100000
9/26/91	1000		
9/30/91	4000000		2400000
10/1/91	800000		1800000
10/8/91			2000000
10/9/91	1100000		
10/17/91	12800000		6400000
10/24/91	2950000		
11/11/91	1800000		1700000
11/12/91	350000		390000
11/13/91	240000		300000
11/14/91	590000		650000
11/15/91	200000		220000
11/16/91	970000		7100000

CHLORINE DIOXIDE SYSTEM START-UP

HYDROGEN PEROXIDE START-UP (160ppm)

HYDROGEN PEROXIDE (20ppm)

HYDROGEN PEROXIDE STOP

HYDROGEN PEROXIDE START-UP (20ppm)

Era Laboratories, inc.
North 21st Avenue West
Duluth MN 55806-2017 (218)727.6380

TABLE 3 (continued)

LABORATORY REPORT

Hennepin Paper Company
Attn: Wastewater Operator
Lindberg Drive
Little Falls, MN 56345

LAB NO: 111525
DATE REC'D: Nov. 26, 1991
DATE/REPORT: Dec. 12, 1991

HETEROTROPHIC PLATE COUNT per mL

#13 Mill Hose, rec'd 11/26/91	980,000
#14 ZDS, rec'd 11/26/91	2,000,000

ERA LABORATORIES, INC.


Robert D. Magnuson

Era Laboratories, Inc.
24 North 21st Avenue West
Duluth, MN 55806-2017 (218)727.6380

TABLE 3



LABORATORY REPORT

Hennepin Paper Company
Attn: Wastewater Operator
Lindberg Drive
Little Falls, MN 56345

LAB NO: 111163-111391
DATE REC'D: Nov 12-Nov 20
DATE/REPORT: Nov. 26, 1991

HETEROTROPHIC PLATE COUNT per mL

#1 Mill Hose, 11/11/91 @ 1015	1,700,000
#2 ZDS; 11/11/91 @ 1025	1,800,000
Mill Hose #3, 11/12/91	390,000
ZDS #4, 11/12/91	350,000
Mill Hose #5, 11/13/91	300,000
ZDS #6, 11/13/91	240,000
Mill Hose #7, 11/14/91	650,000
ZDS #8, 11/14/91	590,000
#9 Mill Hose, 11/18/91 @ 1315	7,100,000*
#10 ZDS, 11/18/91 @ 1315	970,000
#11 Mill Hose, 11/19/91 @ 1330	150,000
#12 ZDS, 11/19/91 @ 1335	9,000,000*

*Estimate

ZD5= zero Discharge sump

ERA LABORATORIES, INC.


Robert D. Magnuson

Era Laboratories, Inc.
24 North 21st Avenue West
Duluth, MN 55806-2017 (218)727.4380

T A B L E 2



L A B O R A T O R Y R E P O R T

Hennepin Paper Company
Attn: Wastewater Operator
Lindberg Drive
Little Falls, MN 56345

LAB NO: 109791-110033
DATE REC'D: Sept 26-Oct 2
DATE/REPORT: Oct. 10, 1991

HETEROTROPHIC PLATE COUNT per mL

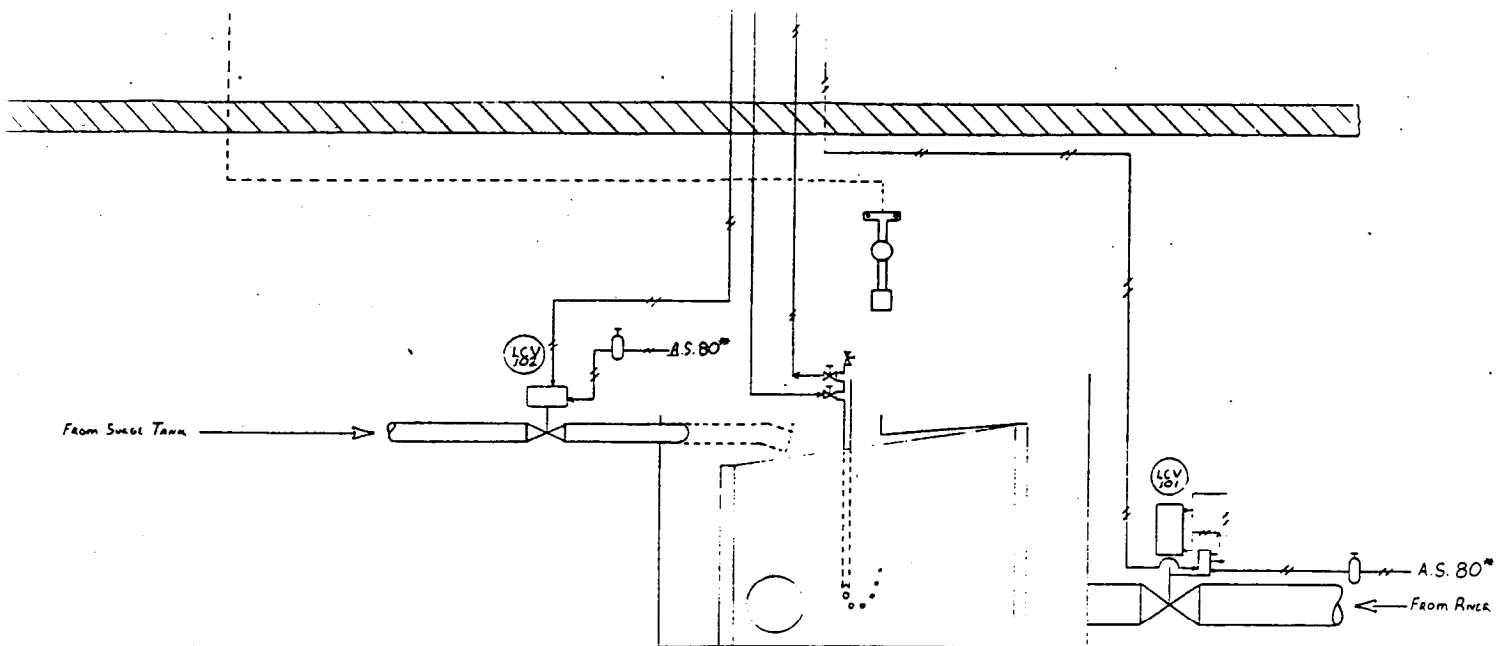
Hose Mach #1, 9/25/91	3,100,000*
Parshal #2. 9/25/91	3,600,000*
Mill Hose #3, 9/26/91	250,000
Parshall #4, 9/26/91	160,000
Mill Hose #5, 9/26/91	6,100,000*
Parshall #6, 9/26/91	5,900,000*
Mill Hose #7, 9/30/91	2,400,000
Parshall #8, 9/30/91	4,000,000
Mill Hose #9, 10/01/91	1,800,000
Parshall #10, 10/01/91	800,000

*Estimate

Parshall is equivalent to Zero discharge Sump

ERA LABORATORIES, INC.


Robert D. Magnuson



CONTROL LOOP DATA

TYPE

FORBORD 43AP 3-15 PSI 0-48" H₂O

MILLER FLUID POWER LAS3H4N MOORE POSITIONER SERIES 74 AIR TO CLOSE 1/4"

ENTERRA 7860 4-20 MA

FORBORD 43AP 3-15 PSI 0-48" H₂O

GRINNEL SERIALS 8000 MOORE POSITIONER MODEL 750P AIR TO OPEN 8"

FORBORD M/40 PR 3-15 PSI

Figure 7

REV. NO.	DATE	BY	REMARKS
DRAWN BY			MILL FRESHWATER SUPPLY CHEST CONTROL LOOP CONFIGURATION/ SURGE TANK
TRACED BY			
CHECKED BY			

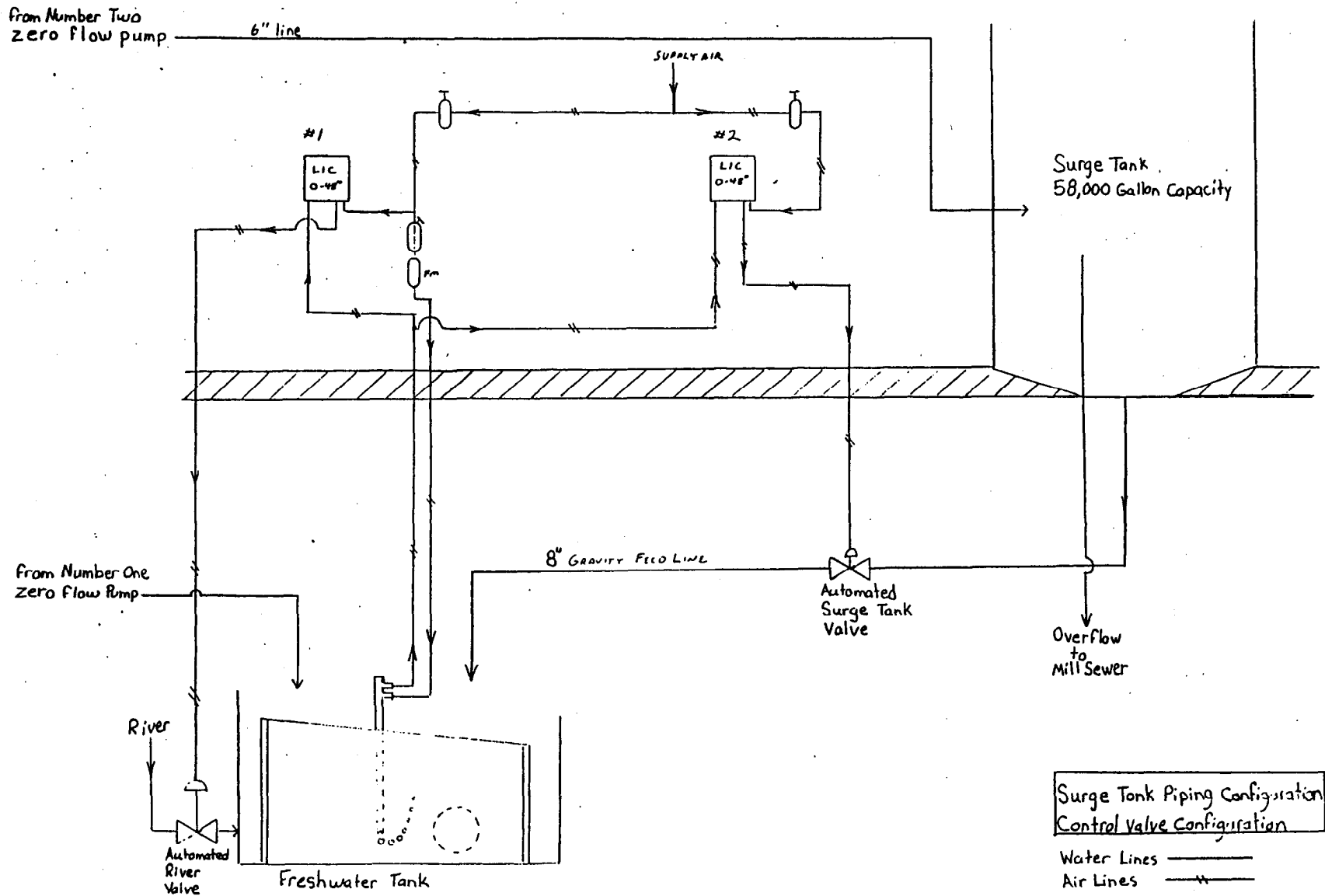


FIGURE 6

02 DISCHARGE VS CITY WATER USAGE

MONTHLY AVERAGES, JUNE 1990-JUNE 1991

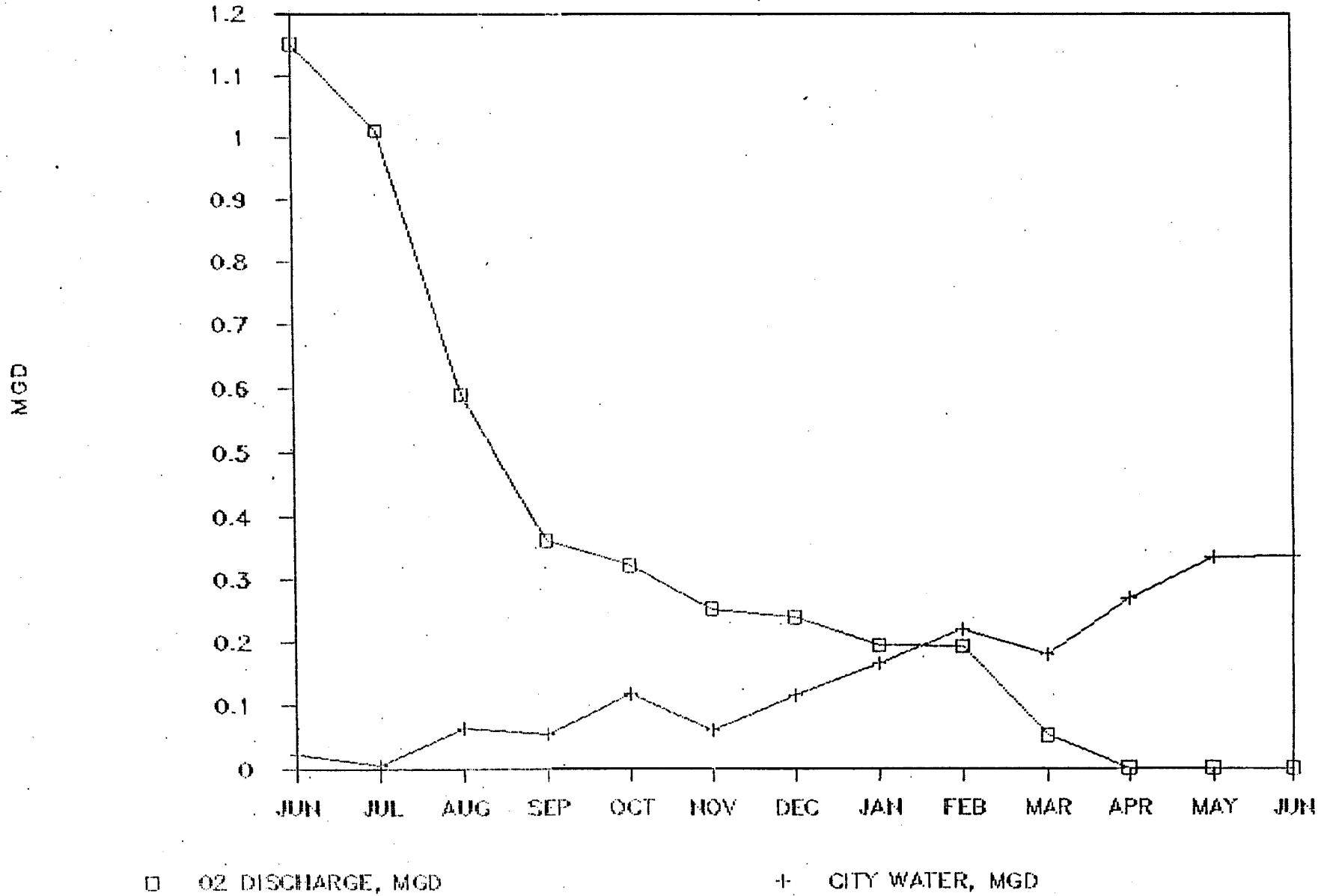
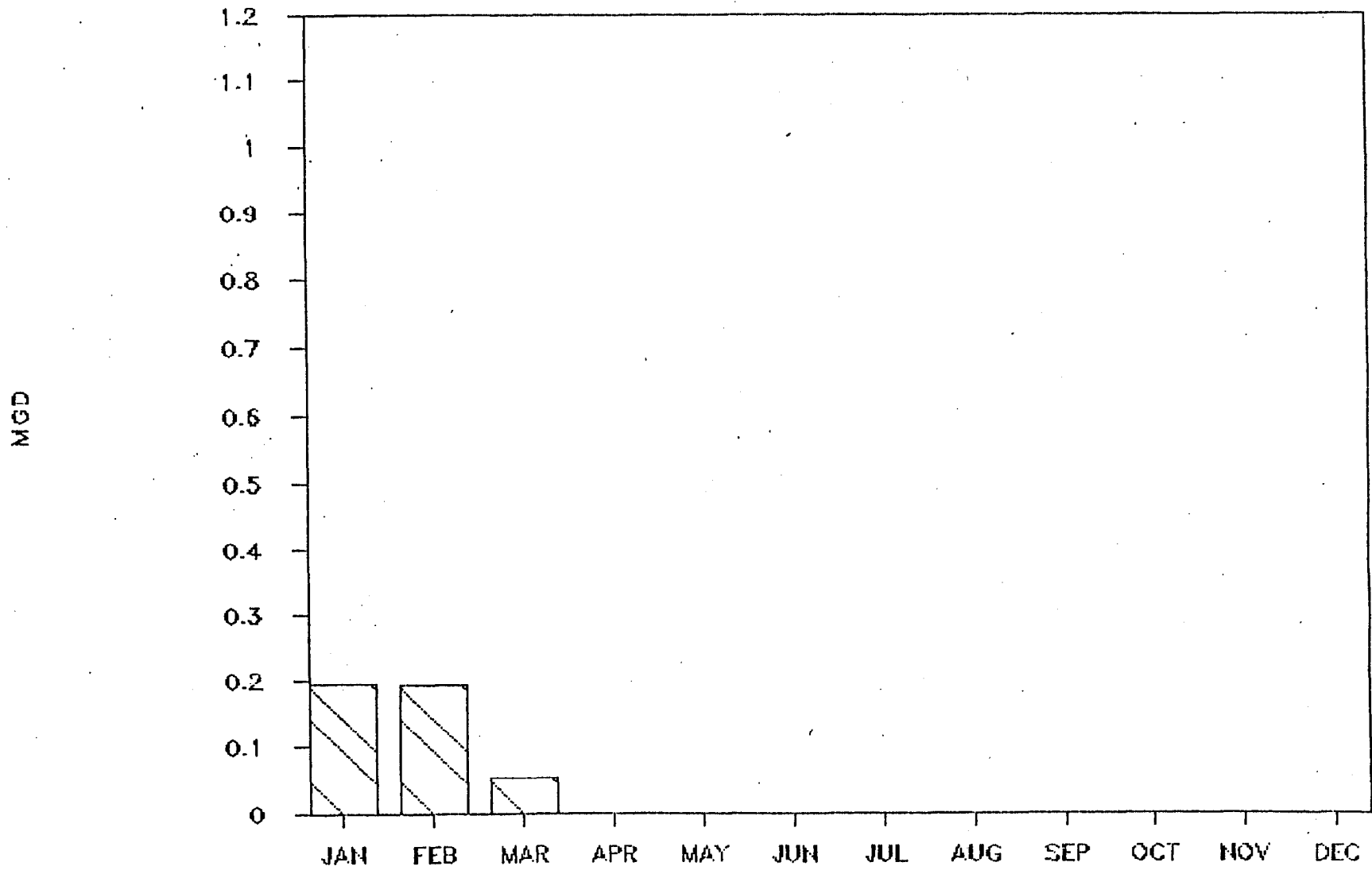


FIGURE 5

O2 EFFLUENT DISCHARGED

MONTHLY AVERAGE 1991



02 EFFLUENT DISCHARGED

MONTHLY AVERAGE 1990

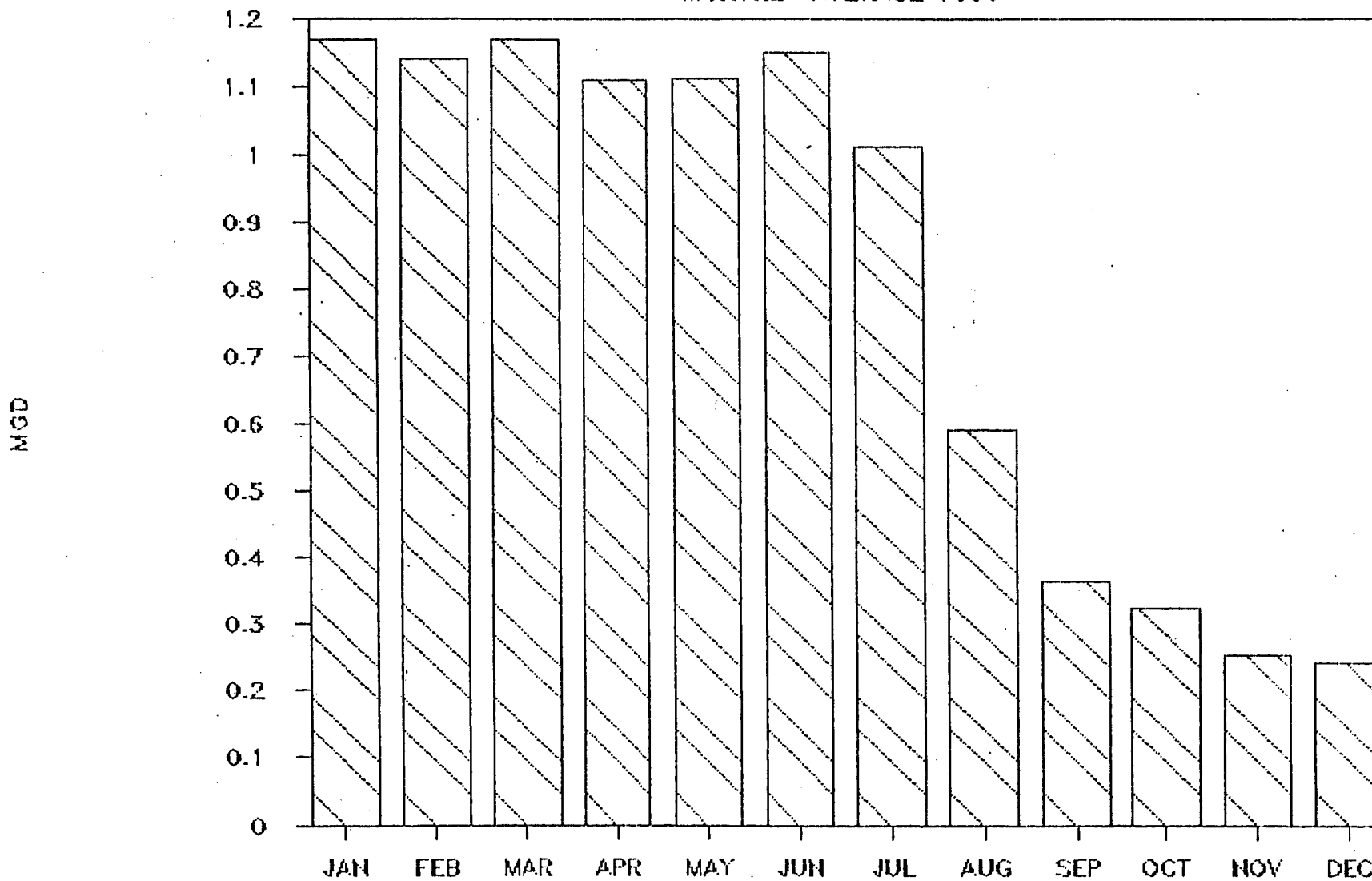


FIGURE 3

01 EFFLUENT DISCHARGED

MONTHLY AVERAGE 1991

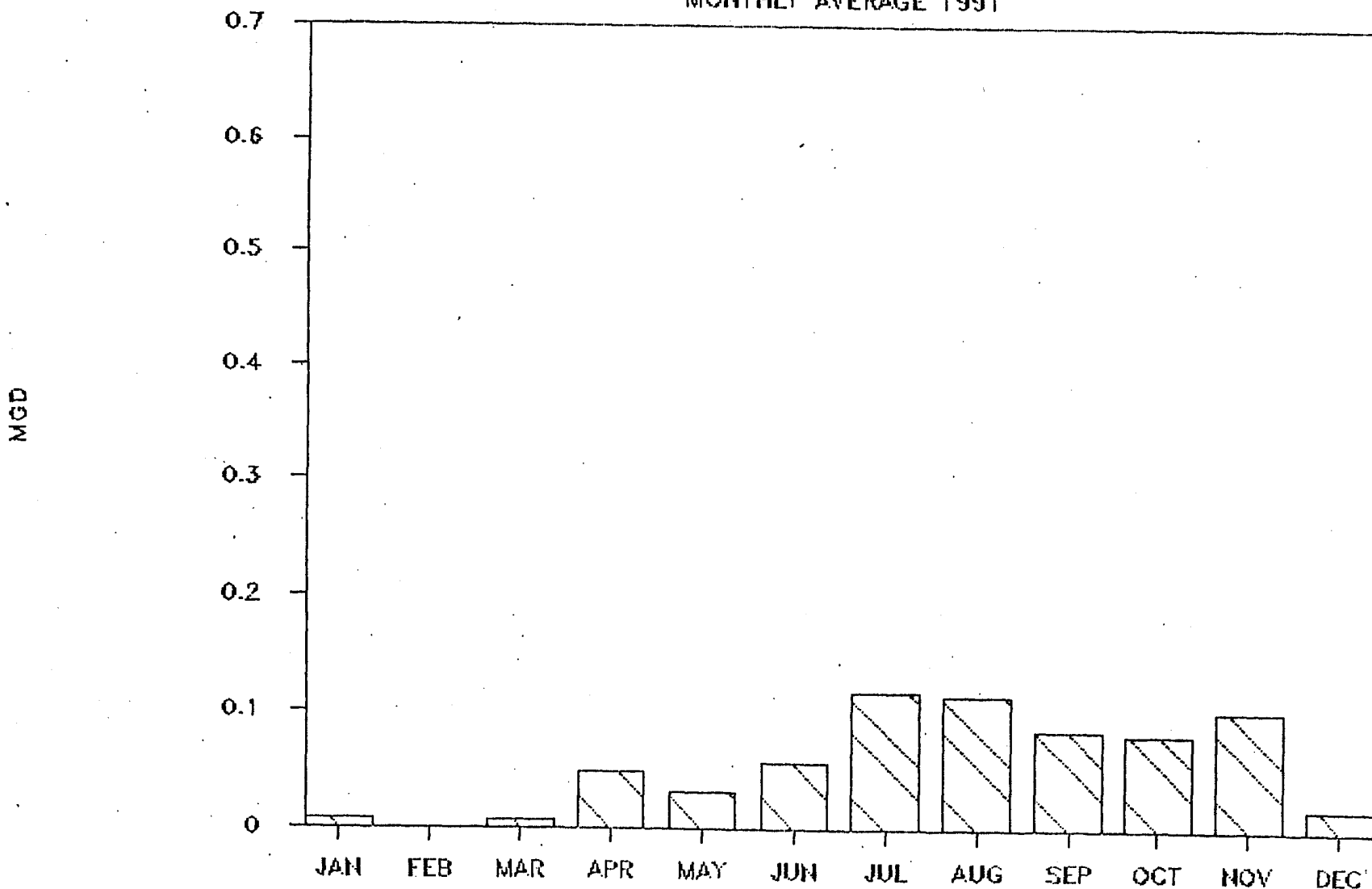


FIGURE 2

01 EFFLUENT DISCHARGED

MONTHLY AVERAGE 1990

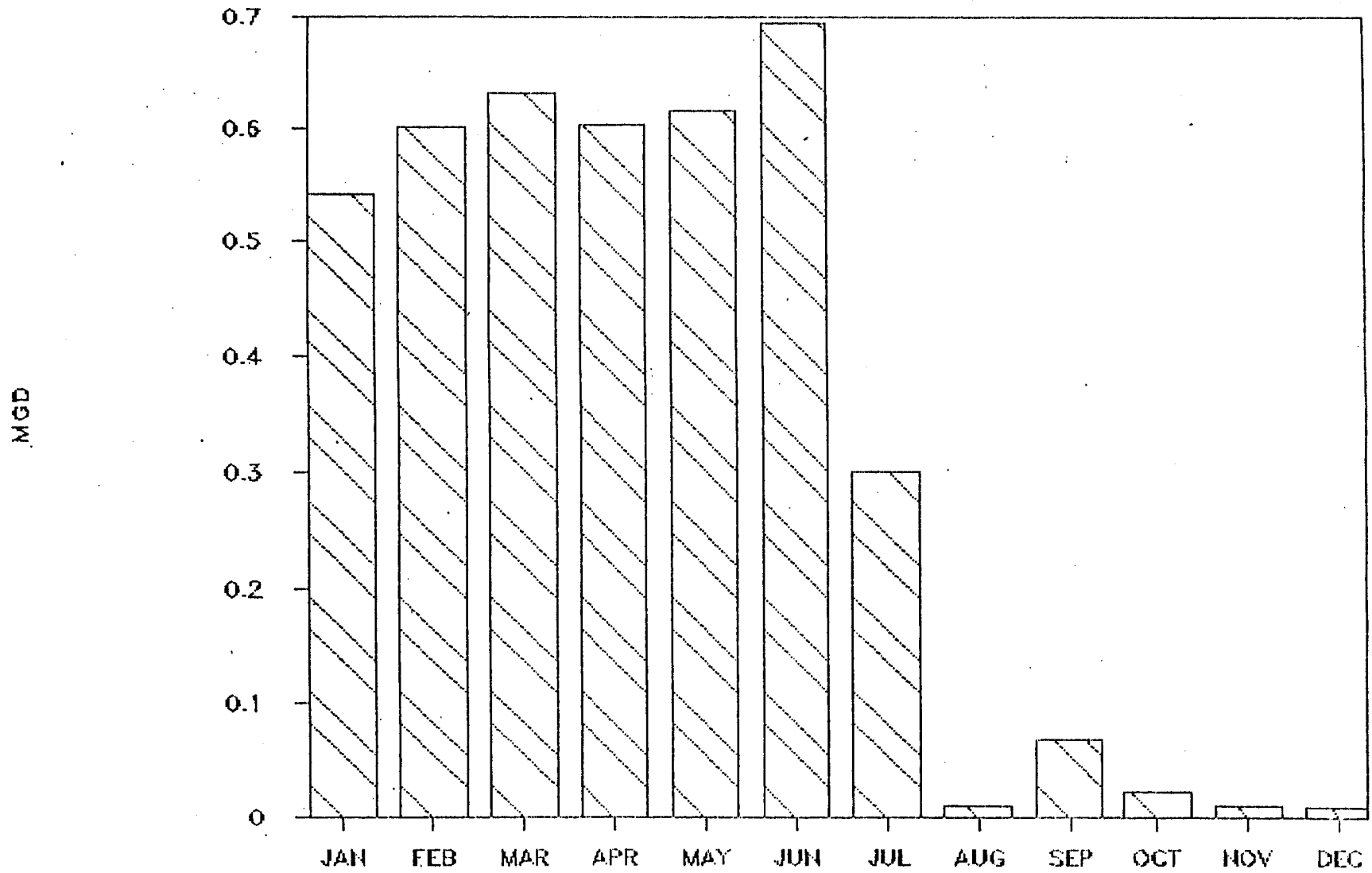


FIGURE 1

PROJECT EXPENDITURES

To date, \$8,601.92 has been expended on this Pollution Prevention Project. The costs break down as follows:

	TOTAL	STATE FUNDS	MATCHING FUNDS
Labor	\$3,373.50	\$3,373.50	.00
Materials	4,277.00	.00	\$4,277.00
Testing	312.00	312.00	.00
Miscellaneous	639.42	639.42	.00

Invoices available at the time of writing are attached as Appendix A. Invoices for toxicity testing performed by Integrated Paper Services, Inc. have not been received at the time of this writing.

COMMENTS AND CONCERNS

To date the project has proceeded smoothly. Except for one delay in laboratory testing, every task has been completed on schedule. We look forward to continuing our work on this project.

Page 8

Zero Discharge Program
Hennepin Paper Company

With data gathered from Task 2 study of zero discharge pumping and piping systems, it was determined that a surge tank coupled with increased pipeline diameter from the number two zero flow pump to the surge tank would result in fewer discharges to the Mississippi River. Since this system became operational, 63% of the days have had zero discharge to the Mississippi River.

It is concluded that with more efficient waste water treatment, a higher quality waste water would be available for recycling. Some form of waste water filtration, coupled with an effective microbial control program, should allow for continued reuse of waste water.

Bench testing of Waste Water Treatment Plant influent was done in order to simulate the effects primary clarification might have on the waste water. A sample of waste water influent was split into two samples of equal volume. One sample received no treatment while the other was filtered through coarse filter paper (Whatman Grade 202) to remove wood fibers. An oxygen consumption rate test was performed on each sample (Standard Method 2710B, 17th ed.). The specific oxygen consumption rates for the unfiltered and filtered sample were 6.45 and 22.13 mg/g/hour respectively. This shows that waste water with primary clarification should degrade faster than that with no primary clarification.

The unfiltered and filtered influent samples were analyzed for Total Suspended Solids (T.S.S.), Volatile Solids (V.S.) and Biochemical Oxygen Demand (B.O.D.). The following data show the results and percentage reduction achieved by simple filtration.

	Unfiltered Influent	Filtered Influent	% Reduction
T.S.S. (mg/L)	1,423	584	59
V.S. (mg/L)	772	225	71
B.O.D. (mg/L)	499	416	17

The reduction in suspended solid is due mainly to the removal of wood fiber. The chief constituent of wood fiber is cellulose which cannot be decomposed given the time and conditions in the Waste Water Plant.. Removal of this fiber would allow for more efficient biological treatment. Volatile solids represent an approximation of the amount of organic matter in the sample. Filtration greatly reduces the volatile solids in the waste water. A reduction in BOD is also realized.

Project Results

Results obtained from Task 1 show that since the inception of the Zero Discharge Program, much pollution prevention has been achieved in the form of decreased discharges of waste water to the Mississippi River. Linked to these desired results -is the deleterious effect of the recycled waste water on the mill's pumping and piping systems.

Results of Task 2 show that both chlorine dioxide and' hydrogen peroxide can effectively relieve the biofouling of the mill's piping systems. It has been determined that the effect of biological growth within pumps. and piping is of more concern than the clay suspended in the recycled water.

It has been shown that economically feasible doses of hydrogen peroxide and chlorine dioxide have no effect on waste water toxicity. Powdered activated carbon treatment did show a reduction in waste water toxicity.

dioxide normally fed at 2 ppm). This concentration of peroxide was a slug dose to try to bring the system count as low as possible. After twenty-seven hours, the dosage was lowered to 20 ppm. The point of addition for all disinfectants is just before the zero flow pumps. Hydrogen peroxide was fed for eight days and samples for heterotrophic bacterial plate counts were taken on five days. Two sampling points were utilized: one at the zero discharge sump, and the other at the paper machine wet end hose (designated "mill hose"). The results of these bacterial plate counts are presented as Table 2.

On November 11, 1991, chlorine dioxide was again replaced by hydrogen peroxide. No slug dose was utilized and the feed rate was 20 ppm. This trial ran for fourteen days, and bacterial plate count samples were taken on seven days. The results are found in Table 3.

Three waste water samples were submitted for toxicity testing, a blank containing no hydrogen peroxide, one dosed with 20 ppm hydrogen peroxide, and one dosed with 100 ppm hydrogen peroxide. This was done to determine if the material responsible for waste water toxicity could be oxidized and rendered non-toxic by the hydrogen peroxide. The test organism used was *Ceriodaphnia dubia* and the test procedure was time to lethality. There were no differences in time to lethality between the three samples.

Table 4 presents the results of bacterial plate counts over time. Counts have fluctuated a great deal, however, since the chlorine dioxide disinfection system has come on line, some relief in plugging of pipes has been realized. The second hydrogen peroxide trial showed decreased plate counts compared to counts obtained immediately prior to trial start-up when chlorine dioxide was being used.

In order to determine if chlorine dioxide is able to reduce the toxicity of the water, three samples were submitted for time to lethality testing as previously described. These samples consisted of a blank (no chlorine dioxide added), and two dosed with 3 ppm and 25 ppm each. There were no differences in time to lethality between the three samples. The blank sample was then treated with powdered activated carbon (P.A.C.). P.A.C. has the ability to absorb many organic molecules. This treatment extended the time to lethality from approximately six hours to over forty-eight hours.

Hennepin Paper Company's Waste Water Treatment plant does not have a primary clarifier, therefore, significant amounts of wood fiber pass directly to two aeration tanks for biological treatment. It is hypothesized that if some of this organic loading could be eliminated from the Waste Water Treatment plant, then more efficient biological treatment would result which would produce a higher quality waste water for recycling.

This flow meter was used to determine the throughput of the Waste Water Treatment Plant, and from this information it was determined that approximately 1,200 gallons per minute of pumping capacity would be needed in the zero discharge sump in order to handle normal flow, plus surges. Data from the number one and two zero discharge pumps showed flow rates of 240 and 390 gallons per minute respectively. These two pumps are similar models, and from studying their performance curves it could be seen that the total dynamic head placed on these pumps was causing low flow rates.

At this time, a surge tank became operational. A surge tank was needed to prevent waste water from overflowing the freshwater tank and reentering the waste water system. It was observed that at times the freshwater tank would overflow and, shortly thereafter, demand on the house pump would return and river water would be introduced to the freshwater tank through the automated river valve. By placing a surge tank between the number two zero flow pump and the freshwater tank, the waste water which would normally overflow could now be held in reserve until the house pump demand increased. An automated valve between the surge tank and the freshwater tank controls the flow of water out of the surge tank. The water level in the freshwater tank controls the valve. The river water valve and the surge tank valve are adjusted so that the surge tank valve will open first once the level in the freshwater tank drops. If the surge tank cannot supply an adequate volume of water, the river valve will open and river water will fulfill the demand.

The number two zero flow pump supplied water to the surge tank through a four inch pipe at 390 GPM. It was realized that although the surge tank system was working as planned, the number two zero flow pump did not have the capacity to prevent discharges to the River. The tortuous route of the piping from the number two zero flow pump to the surge tank caused excessive head to be placed on the pump. For this reason, a new six inch pipe was routed more directly to the surge tank. With this pipe in place, the flow rate from the number two zero flow pump increased from 390 GPM to 900 GPM, thereby greatly reducing discharges to the River.

Figure 6 illustrates the surge tank piping and control valves configurations. Figure 7 shows the control loop configuration.

Treatment technologies to improve the quality of the recycled waste water were studied. In May, 1991, a chlorine dioxide generation system was installed to combat the microbial growth problems within the mill. As part of Task 2, hydrogen peroxide was compared to chlorine dioxide for effectiveness of bacterial control and reduction of waste water toxicity.

On September 25, 1991, the chlorine dioxide was shut off and hydrogen peroxide was fed into the recycled waste water at 150 ppm (chlorine

water. As explained earlier, this usage of city water only added water to the closed system and caused increased discharges to the River. Several different types of spray nozzles were investigated in order to find a design which would allow the use of recycled waste water. A non-plugging design was purchased and the shower nozzles were replaced which now allows recycled waste water to be used once again as a shower water source on this piece of equipment.

Project Status and Procedures - Task 2

Task 2 involved investigating potential treatment technologies which will allow continued reuse of waste water. Also, investigation of pumping and piping systems which would allow for sustained zero discharge was conducted.

Waste Water Treatment plant effluent is intercepted by three pumps, termed zero flow pumps, located in sumps immediately upstream from outfall 01. These pumps are numbered one, two and three. Prior to the onset of this Pollution Prevention Grant Study, both the number one and number two pumps delivered waste water to the freshwater tank via four inch PVC pipes. The number three pump provides makeup water to the Pulpmill. Still, with all three pumps operating, their capacity was not enough to prevent discharges to the River.

In order to determine what type of pumping and piping system could prevent all discharges to the River, data was collected in order to complete a water balance for the entire mill system. Obtaining data on water inputs and outputs was quite difficult due to the lack of flow measurement devices on many pipes. One of the most difficult flows to measure was the volume of waste water recycled through the system each day. Because of the required placement of the zero flow pumps prior to the 01 outfall, the open channel flow meter which previously measured Waste Water Treatment Plant discharge, now only measured that volume of water which the pumps could not handle and is discharged. No flow meters were present in the pipes carrying waste water from the zero discharge pumps. Based on observations, it was known that if additional zero discharge pumping capacity was added, it could not all be directed to the freshwater tank because the demand for water within the mill dictates how much water is needed. If excess waste water would be directed to the freshwater tank it would overflow the tank and return to the Waste Water Treatment Plant. Still, flow measurements were needed to size any changes in the pumping and piping system.

To facilitate the acquisition of flow measurements without extensive downtime and costs associated with the purchase of individual flow meters, a non-intrusive ultrasonic transit-time flow meter was purchased (Panametrics Model 6068). This flow meter can be strapped to the outside of nearly any pipe and accurate flow measurements obtained.

Zero Discharge Program
Hennepin Paper Company

since implementation, the average daily load application has been 1.26. This represents an increase of 23%, however, this does not necessarily translate into a 23% increase in sludge volume because load sizes may vary from 15,000 pounds to 30,000 pounds. It is correct to say that an increase has been realized since the Zero Discharge Program was implemented, but it is not possible to absolutely quantify the increase.

Several problems in manufacturing operations have arisen as a result of the Zero Discharge Program. One of the first problems encountered was dealing with colored waste water. Hennepin Paper Company manufactures Colored Construction Paper, therefore, the treated waste water has some degree of color. Manufacturing of the various colors had to be arranged so the color of the water would not cause the quality of the product to be degraded. It was found that a sequence starting with lighter colors could progress into deeper and darker colors culminating in black. After black, successively lighter shades are made such as grays, browns or blues, and finally ending up with white. This color sequence manufacturing has gone through has had several evolutions and refinements and will undoubtedly be refined further in the future.

Several maintenance problems have arisen as a result of the Zero Discharge Program. The most common problems are pipe and shower plugging and increased wear on pumps. These problems have caused the cost of maintenance material and labor to increase. Since the programs implementation, maintenance labor costs have increased an average of 32% per month while maintenance materials cost has increased 145%. A portion of the materials cost reflects expenditures for equipment for the Zero Discharge Program. In many instances pumps and piping runs have been replaced, and replacements will continually have to be made due to the decreased service life caused by the recycled waste water. Shell and tube heat exchangers used to condense steam from the paper machine dryers have had to be taken out of service on five different occasions due to fouling caused by recycled waste water being used for cooling water.

It has been determined that nearly all of the pipe and shower plugging resulted from biological growth, particularly slime forming bacteria. Although suspended clay particles in the water may shorten the life of pumps, the slime growth problem demanded immediate attention. In May, 1991, a chlorine dioxide disinfection system was installed. This system has greatly alleviated the problem of pipe plugging. Fine nozzle showers did however continue to plug.

The belt filter press used for dewater waste treatment sludge has three shower pipes consisting of approximately fifteen spray nozzles across the six foot long pipe. These nozzles were plugged continuously, even with a fine mesh filter upstream. To alleviate the problem, the water supply was switched from recycled water to city

Prior to implementation of the Zero Discharge Program, 100% of the mill's process and cooling water was supplied by the Mississippi River. This water entered the mill and passed over a fine mesh screen termed the freshwater screen. This screen is placed over a 2,700 gallon concrete tank termed the freshwater tank. A pump termed the house pump, delivers water from the freshwater tank to all of the process and cooling water demand points throughout the mill. Upon initiation of the Zero Discharge Program, waste water was pumped from the 01 outfall to the freshwater tank. An automated valve placed in the incoming river water line is controlled by the level of water in the freshwater tank. If the volume of waste water supplied to the freshwater tank is not sufficient for the demand of the house pump, then this automated river valve will open to fulfill the demand. Conversely, if the supply of waste water delivered to the screen was in excess of house pump demands, this waste water would overflow the freshwater tank and reenter the waste water treatment system. By pumping increasing amounts of treated waste water to the freshwater tank, the mill's process and cooling water became nearly 100% recycled waste water. This fact is what caused, and is still causing, maintenance and manufacturing difficulties within the mill. Some of the maintenance problems were solved by simply eliminating the use of recycled waste water and using city water. The 01 outfall discharges throughout 1991 are a direct result of increased city water usage.

The decrease in volume of waste water discharged translates into a reduction of pollutants released to the environment or pollution prevention. Table 1 illustrates the pollution prevention achieved through November, 1991 by comparing the sixteen months before the initiation of the Zero Discharge Program (March, 1989 - June, 1990) to the sixteen months the program has been in place (August, 1990 - November, 1991).

TABLE 1
 POLLUTION PREVENTION RESULTING FROM ZERO DISCHARGE PROGRAM

	WATER DISCHARGED	SOLIDS DISCHARGED	BOD DISCHARGED
Before:	853.711 Million Gallons	188,956 Pounds.	97,400 Pounds
After:	90.095 Million Gallons'	33,603 Pounds	56,979 Pounds
R e d u c t i o n :	89.4%	82.2%	41.5%

Based on an average operating year, the Zero Discharge Program has eliminated releases to the Mississippi River totaling 572,712,000 gallons of waste water, 116,515 pounds of total suspended solids, and 30,315 pounds of biochemical oxygen demand.

The amount of waste water sludge that has been land applied has increased slightly since the implementation of the Zero Discharge Program. For the sixteen months preceding the program, an average of .97 loads of sludge was land applied per day. In the sixteen months

INTRODUCTION

Hennepin Paper Company manufactures primarily colored Construction Paper at a paper mill in Little Falls, Minnesota. The mill is located on the west bank of the Mississippi River, and has been in operation since 1890. In July, 1990, Hennepin Paper Company initiated a Pollution Prevention Program termed Zero Discharge. The goal of this program is to eliminate all discharges of waste water to the Mississippi River by recycling that water back into the manufacturing process.

The first task of this study aims to quantify the impacts of the Zero Discharge Program from both environmental and manufacturing perspectives. The second task involved investigation and preliminary testing of various treatment technologies which will allow continued reuse of waste water in the manufacturing process.

Project Status and Procedures - Task 1

'At the onset of the Zero Discharge Program, waste water was discharged to the Mississippi River through two outfalls. Outfall 01 discharged process waste water, and outfall 02 discharged cooling water. Figures 1 and 2 show average daily 01 outfall discharge for, each month of 1990 and 1991 respectively. Prior to initiation of the Zero Discharge Program, an average of 607,000 gallons per day of process waste water was discharged. Since July, 1990, the discharges of process water to the River have varied. Figures 3 and 4 illustrate average daily 02 outfall discharges for 1990 and 1991 respectively. The discharges through outfall 01 are impacted by the decrease in 02 outfall discharges. Prior to July, 1990, an average of 1.140 million gallons per day was discharged through outfall 02. As part of the Zero Discharge Program, this waste cooling water was diverted to the process sewer and treatment system. In January. and February of 1991, approximately 200,000 gallons per day of waste cooling water was still being discharged. On March 8, 1991, the total volume of waste cooling water was diverted to the process water system. This caused an increase of discharges through outfall 01 due to the increased volume of water in the process waste water treatment system. This increase can be seen beginning in the month of March., 1991 in Figure 2.

Coupled with the absorption of all the cooling water into the process water system was an increased 'use of city water within the mill. It was found that the recycled waste water was not suitable for use as cooling water on some pieces of critical equipment. Also, critical showers on the paper machine were converted to city water, both areas adding water to the waste water system. Figure 5 shows the correlation between 02 outfall discharge and city water usage for June, 1990 through June, 1991.

ZERO DISCHARGE PROGRAM
AT AN UNCOATED GROUNDWOOD PAPER MILL
PROGRESS REPORT

BY

Ronald T. Klinker
Environmental Affairs Manager
Hennepin Paper Company
100 Southwest Fifth Avenue
Little Falls, Minnesota 56345

December 20, 1991

This project is funded through a Pollution Prevent Grant from:

The Minnesota Office of Waste Management
1350 Energy Lane
Saint Paul, Minnesota 55108

Grant Program Contact:

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Pollution Prevention Grant Program
Minnesota Office of Waste- Management
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APPENDIX 1

Parameters For Hennepin Paper Company Mill Simulation

1) Greenwood Preparation	
a) Grinder pit pulp consistency	<u>2.5-3.0</u>
b) Grinder pit temperature	<u>130°F</u>
c) Pulp freeness, CSF	
d) Nalco Nalcon 7620-WB Microbiocide	0.096 g/lb pulp
e) Nalco 7613 Dispersant	0.461 g/lb pulp
f) Dumar DM-40-AD4 Defoamer	0.491 g/lb pulp
2) Furnish Repulping and Mixing	
a) Pulp blend	50% Poplar GW 20% kraft 30% secondary
b) Slurry consistency	<u>4.5-5.0</u>
c) Temperature	<u>120°F</u>
d) Retention time	<u>1 hr</u>
3) Bleaching of Mixed Stock	
b) Initial pH, (adjust with NaOH)	8.0
c) Temperature	115° F
d) Retention time	90 minutes
e) Slurry consistency	<u>4.5-5.0</u>
f) Bleach liquor composition:	
Water	90.5%
Sodium silicate (35-40%)	3.1%
Sodium Hydroxide (50%)	3.1%
Hydrogen-peroxide(50%)	3.3%
g) Bleach liquor addition	0.12 gal/lb fiber
	Lower pH of stock to 6-7 after 90 minute retention.
4) Pulp Beating	
a) Slurry consistency	<u>4.5-5.0</u>
b) Target freeness, CSF	<u>160</u>
c) Color	7.30 g/lb furnish
d) Alum.	31.7 g/lb furnish
e) Approximate beating time	<u>10 minutes</u>
5) Machine chest	
a) Ogilvie Cato 15 Starch	4.99 g/lb furnish
b) Slurry consistency	<u>4.5-5.0</u>
c) Temperature	<u>120°F</u>
d) Retention time	<u>15 minutes</u>
6) Paper Machine White Water System	
a) Henke Foamaster DF-212	0.80 g/lb furnish
b) Slurry consistency	<u>.25</u>
c) Temperature	<u>100-110°F</u>

ATTACHMENT 2

INTER-OFFICE CORRESPONDENCE
HENNEPIN PAPER COMPANY'
March 25, 1992

TO: File

FROM: Ron Rlinker

SUBJECT: Powdered Activated Carbon Treatment of Wastewater Effluent

On March 23, 1992, a sample of wastewater effluent was grabbed from the zero discharge sump. One gallon of this sample was transferred to a one gallon cubitainer supplied by Environmental Monitoring, Inc. A second one gallon sample was treated with 1000 ppm powdered activated carbon (Baker Decolorizing), mixed thoroughly and allowed to stand for one hour. The carbon was removed from the water by successive filtration through 15 micron (Reeve Angel Grade 202) filter paper and 1.5 micron (Whatman Grade 934-AH) glass fiber filters. This carbon treated sample was placed in a second cubitainer. These samples were then shipped to E.M.I. for timed lethality toxicity testing (c. dubia).

Subjectively, the P.A.C. treatment removed 95% of the color in the sample. The wastewater effluent had a T.S.S. concentration of 152 ppm and a pH of 6.9. The P.A.C. treated sample had a pH of 7.2.

de

INTER-OFFICE CORRESPONDENCE
HENNEPIN PAPER COMPANY
April 14, 1992

TO: File

FROM: Ron Klinker

SUBJECT: Granular Activated Carbon Treatment
of Waste Water Effluent

A Whatman Carbon-Cap activated carbon filter unit has been obtained for bench scale waste water treatment toxicity reduction studies. This unit contains .015 cubic feet of carbon. An important parameter in carbon filtration is the empty bed contact time (EBCT) which is the volume of carbon contained in the filter unit divided by the flow rate. Longer EBCT provides for greater treatment.

On April 10, 1992, the carbon cap was put into service by flushing out fines with three liters of distilled water. After this, 1.5 liters of effluent were passed through the filter. The effluent was pink with a TSS concentration of 77 mg/L. After passing through the column the color was 100% removed. Some suspended material remained, however much less than the original sample. The EBCT was .28 minutes.

On April 13, 1992, 4 liters of effluent were passed through the filter with an EBCT of .55 minutes. The treated effluent was then placed in a one gallon cubitainer and sent to EMI Labs for timed lethality toxicity testing on c/ dubia. A one gallon sample of effluent not treated with carbon was also shipped for baseline information. The initial pH and temperature of the samples was 7.2 and 76 F. The TSS concentration of the sample was 66 mg/L. The water was bright red prior to filtration and after one pass through the filter the water was a very light red. After a second pass through the filter, only a slight hint of red remained. By decreasing the flow rate through the filter, color could be 100% removed. If the EBCT were increased, a gin clear effluent could be achieved.

de

Mill Simulation and Toxicity Tests For
Hennepin Paper Company
Little Falls, Minnesota
May 6, 1992

(IPS Project 5049)

INTRODUCTION

This report presents the results of a laboratory simulation of mill processes and subsequent toxicity tests on laboratory generated wastewaters. This study was conducted by Integrated Paper Services, Inc. on behalf of Hennepin Paper Company in an attempt to (a) identify the cause(s) of toxicity in Hennepin Paper's mill wastewater, and (b) recommend possible solutions to the toxicity problem.

METHODS

Mill conditions were provided by Hennepin Paper Co. and duplicated as best possible in the laboratory. Toxicity tests on the generated wastewaters followed the Time-to-Lethality format used in previous toxicity studies for Hennepin. Laboratory methods expanded on those proposed and included mill simulations in two different process waters and a simulation without bleached stock.

MILL PROCESS SIMULATION

All components, with the exception of water, necessary for mill simulation were provided by Hennepin Paper Company (1). The conditions for this study were chosen to simulate actual mill conditions at Hennepin Paper Company; some, however, were slightly modified due to equipment limitations (Table 1).

Groundwood pulp was produced in a Sprout-Waldron 10" single disk refiner. The freeness of the pulp produced was lower than the mill specifications. This lower freeness should not have affected the toxicity of this pulp. Other variations were lower process temperature and lower consistency in the valley beater.

River water, as originally proposed, was not used as the process water. Equipment limitations (refiner) and volume constraints proved unfeasible. Instead, the first simulation was conducted using deionized water, and the second and third simulations were conducted using dechlorinated tap water (toxicity lab culture water). These differences were unavoidable and were projected not to compromise the integrity of the study.

Table 1. Mill vs. laboratory process conditions

Process	<u>Mill</u>	<u>Lab</u>
1) Greenwood Preparation		
Consistency, %	2.5-3.0	3.2
Temperature, °F	130	Same
Freeness, ml CSF	300	150
Nalco Nalcon 7620-WB, q/lb pulp	0.096	Same
Nalco 7613 Dispersant, g/lb pulp	0.461	Same
Dumar DM-40-AD4, g/lb pulp	0.491	Same
2) Furnish Repulping and Mixing Pulp blend	50% Poplar GW 20% Kraft 30% Secondary	Same Same Same
Slurry Consistency, %	4.5-5.0	3.2
Temperature, °F	120	90
Retention Time, min.	60	Same
3) Bleaching of Mixed Stock		
Initial pH	8.0	Same
Temperature, °F	115	Same
Retention Time, min.	90	Same
Slurry consistency, %	4.5-5.0	3.2
Bleach liquor addition, gal./lb	0.12	Same
Lower pH of stock to 6-7 with H ₂ SO ₄		
4) Pulp Beating		
Slurry consistency, %	4.5-5.0	1.8
Target freeness, CSF	160	150
Color,; g/lb	7.30	Same
Alum, g/lb	31.7	Same
Approx. beating time, min.	10	30
5) Machine Chest		
Ogilvie Cato 15 Starch, g/lb	4.99	Same
Slurry Consistency	4.5-5.0	1.8
Temperature, °F	120	90
Retention time, min	15	Same
6) Paper Machine White Water System.		
Henkle Foamaster DF-212, g/lb	0.80	Same
Slurry Consistency, %	0.25	0.3
Temperature, °F	110	80

TOXICITY TESTS

Toxicity tests followed the Time-to-Lethality format used in previous toxicity studies for Hennepin Paper Company. Conditions for the toxicity tests are presented in Table 2. Dissolved oxygen, pH and conductivity, were measured initially and at the end of exposure, i.e., at 48 hours or at the point of complete mortality. Comparison of toxicity results was based on ET50, the time to 50% mortality which is calculated using the graphical method recommended by EPA (2) for LC₅₀ calculation.

Table 2. Test conditions for the time-to lethality tests.

1. Test organism:	Ceriodaphnia dubia (Crustacea: Cladocera)
2. Test type:	Static, non-renewal
3. Age of: test organisms:	Less than 24 hours
4. Test chamber size:	30 mL
5. Test solution volume:	15 mL
6. Renewal of test solutions:	None
7. Replicate chambers/treatment:	2
8. Test organisms/chamber:	5
9. Control water:	Flow-through culture water'
10. Tested concentration:	100% (see Table 3)
11. Temperature:	25 +/- 1° C
12. Feeding regime:	None
13. Aeration:	Groundwood samples initially to raise DO above 40% sat.
14. pH adjustment:	As needed to be within 6.0- 9.0 S.U.
15. Test duration:	48 hours
16. Effects measured:	Mortality (immobilization)

RESULTS

Test controls for all three runs exhibited 100% survival. A summary of organism survival is presented in Table 3.

Table 3. *C. dubia* survival for the mill process simulation runs.

<u>Sample Number</u>	<u>Location</u>	<u>ET₅₀ Values (hours)</u>		
		<u>Run #1</u>	<u>Run #2</u>	<u>Run #3</u>
1	Groundwood	NC	38.0	14.0
2	G.W. + Additives	2.0	NT	4.8
3	Secondary + Kraft	14.0	NT	5.0
4	Post-Bleach	0.7	3.5	NT
5	Post-Color Add.	0.85	1.1	2.1
6	Post-Alum Add.	0.7	2.2	2.3
7	Post-Defoam. Add.	0.85	2.4	2.1
8	1st Pass White H ₂ O	NT	4.0	5.4
9	5th Pass White H ₂ O	2.3	1.4	4.5
10	10th Pass White H ₂ O	2.4	1.4	4.0

NC = not calculable due to less than 50% mortality at 48 hours.
NT = sample not tested

Samples of nos. 1, 5 and 6, during run #2, were filtered through a 1.5 μ glass fiber filter to determine the effects of fines removal. Toxicity in these samples was similar to the unfiltered samples and indicated no physical impairment of organism function in the regular tests (data not here reported). A #9 sample treated with activated carbon at the rate of 1 g/L was also tested during run #2.

Carbon treatment of laboratory produced whitewater resulted in 100% survival at 48 hours of exposure. Run #3 included a sample of culture water adjusted to pH 6.2. This sample was included to measure the potential effects of pH shock (culture pH approx. 8.3). No mortality was observed for the 48 hour exposure period.

CONCLUSIONS

All components used in the papermaking process yielded some toxicity. Groundwood toxicity increased as the sample aged, indicating a leaching of low solubility compounds such as resin acids. Inclusion of the grinder pit additives, defoamer, biocide and dispersant (Sample #2) greatly increased the toxicity of groundwood. The secondary fiber/kraft mix (Sample, #3) exhibited significantly greater toxicity than the groundwood sample.

A post peroxide sample (Sample #4) from the same bleaching run was tested during runs 1 and 2. Toxicity of the sample was higher during the first run probably due to the presence of some unreacted hydrogen peroxide which broke down by the time the second sample was tested one week later. The greatest increase in toxicity (runs #2 and #3) occurred after the addition of the color mixture. Toxicity from the peroxide sample probably masked this toxicity during run #1. Toxicity in the post- alum and defoamer samples remained relatively unchanged from levels in the post-color addition samples.

Whitewater Toxicity was measured on samples collected from the first, fifth, and tenth "passes" through the screen. On the first run, which used deionized water as process water, the first pass white water sample could not be pH adjusted to within 6.0-9.0, presumably because of the low buffering capacity of the sample. Runs 2 and 3 indicated a build-up of the toxicant to a maximum level by the fifth pass. Even though the consistency of white water samples is one-sixth of the color addition samples, toxicity approached similar levels by the fifth pass, indicating a toxicant that either travels with the fiber, or toxicity that is the result of defoamer buildup in the whitewater system.

Defoamer addition to whitewater is approximately 0.7 ppm based on process information provided by Hennepin. Assuming all of the defoamer added stays in the liquid phase, it is possible that defoamer could accumulate to a level comparable to the lower range of LC₅₀ values for similar compounds. The fact that toxicity reaches maximum levels after 5 "passes" rather than increasing as would be-expected if defoamer were the causative agent, suggests a stronger relationship between color and toxicity.

Additionally, toxicity was removed with activated carbon; this suggested adsorption of either an organic compound or a metal which has an affinity for carbon (Sb, As, Bi, Cr, Fl, Br, I, Hg, Pb, or Sn) (4). The carbon data was in agreement with earlier reported work which indicated reduced wastewater treatment plant effluent toxicity following treatment with activated carbon.' The mill simulation avoided the background toxicity. (high dissolved solids resulting in very high conductivity) currently encountered in the effluent,

Further toxicity reduction efforts should focus on either characterization of the toxic component(s) in the color stage or definition 'of minimum levels of activated carbon necessary to achieve to&cant reduction/removal at some point in the system.

Hennepin Paper Company
Project 5049

May 6, 1992
Page 6

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INTEGRATED PAPER SERVICES, INC.

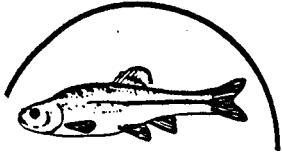
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ATTACHMENT 6



Environmental Monitoring Inc.

P.O. Box 665, New Ulm, MN 56073-0665

Phone (507) 359-1277

Results of a Timed Lethality for Hennepin Paper Co., Little Falls, MN.

A timed lethality toxicity test was conducted for the Hennepin Paper Company beginning March 24 and terminating March 26, 1992. Two effluent-samples were collected on March 23, 1992 using the grab sample method and shipped the same day. Sample #1 is the treated effluent having a pale red color. The second sample, referred to as sample #2, had been treated with 1000 ppm PAC and having no distinguishable color. The collection and measurement of the pH and temperature was performed by Mr. Ron Klinker of Hennepin Paper. After collection a portion of each sample was poured into respective cubitainers, placed into a shipping cooler, covered with ice and sent via Federal Express. The samples arrived March 24, 1992 at 10:26 am. Upon arrival, the temperature of the samples were recorded and pre-test procedures began.

The Ceriodaphnia dubia, raised in moderately hard reconstituted water, used in this test are from in-house cultures. Reference toxicity testing had 'been performed the,

first week of March, which provided data on the healthy condition of the test organisms. Transferring the adult Ceriodaphnia into a fresh medium one day before testing provided less than 24 hour old neonates. The < 24 hour old neonates were collected and placed into a 1 liter beaker containing moderately hard reconstituted water.

Four replicates of 100% sample #1, 100% sample #2 and a moderately hard reconstituted water control were used during the test. Fifteen milliliters of each solution were poured into 30 ml polystyrene cups (test chambers). Water parameter analysis conducted on the effluent samples and control water, include, alkalinity, ammonia, conductivity, dissolved oxygen, hardness, pH, and temperature. The temperature of 25°C was maintained using a recirculating water bath. The test chambers were placed into the water bath and acclimated to the test temperature.. When a stable temperature was reached the initial dissolved oxygen and pH of each solution was recorded. The test began when 5 Ceriodaphnia were randomly placed into each replicate by using a clean glass pipette. A recount was made to ensure that all chambers had five organisms. The test tray was then placed into the water bath, covered with glass and the test initiation time of 11:33 am was recorded.


The methods used for all chemistry analysis were described in ASTM 14th edition. The ASTM method for dissolved oxygen was used to calibrate a YSI model 54A DO meter. The ammonia analysis methods were taken from Orion

Research Inc. owners manuals for the model 720 pH/ISE meter and electrodes for Ammonia. Residual chlorine was not measured.

RESULTS

All observations are documented on the following data sheets. The Sample #1 test organisms began to show signs of toxicity at 12:35 pm. Lethargic organisms were observed under magnification to determine if any movement was present. Using a dissecting scope provided the ability to detect the slightest activity of the organisms appendages. Mortalities began 3 hours and 36 minutes. Organisms in sample #1 died 4 hours and 32 minutes later, at 4:05 pm. Final pH and DO was measured upon termination of the sample #1 test.

For sample #2, toxic effects were observed at 11:36 am on 3/25/92. At this time, several lethargic Ceriodaphnia were observed including 3 deaths. Observations made throughout the day showed increasing mortalities. The following day, 3/26/92, at 8:08 am all remaining Ceriodaphnia were dead. Final pH and DO was measured at termination the sample #2 test.


Allan M. Christensen
Aquatic Toxicologist

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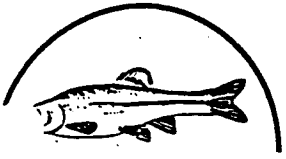
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ATTACHMENT 7



Environmental Monitoring Inc.

P.O. Box 665, New Ulm, MN 56073-0665

Phone (507) 359-1277

Results of a Timed Lethality for Hennepin Paper Co., Little Falls, MN.

A timed lethality toxicity test was conducted for the Hennepin Paper Company beginning April 14 and terminating April 16, 1992. The name of this project is GAC treatment of wastewater. Sample #1 is identified as having a bright red color. Sample #2, showing a slight red tint, had been passed through an activated carbon filter, EBCT = 0.55 min. These two effluent samples were collected on April 13, 1992 using the grab sample method. The collection and measurement of the pH and temperature was performed by Mr. Ron Klinker of Hennepin Paper. After collection a portion of each sample was poured into respective cubitainers, placed into a shipping cooler, covered with ice and sent via Federal Express,. The samples arrived April 14, 1992 at 10:45 am. Upon arrival, the temperature of the samples were recorded and pre-test procedures began.

The Ceriodaphnia dubia, raised in moderately hard reconstituted water, used are from in-house cultures. Transferring the adult Ceriodaphnia into a fresh medium one

day before testing provided less than 24 hour old neonates. These neonates were collected and placed into a 1 liter beaker containing moderately hard reconstituted water. Reference toxicity testing had been performed the first week of April, which provided data on the healthy condition of the test organisms.

Four replicates of 100% sample #1, 100% sample #2 and a moderately hard reconstituted water control were used during the test. Fifteen milliliters of each solution was poured into 30 ml polystyrene cups (test chambers). The test chambers were placed into a 25°C recirculating water bath and allowed to acclimate. When a stable temperature was reached, the initial dissolved oxygen and pH of each solution was recorded. The test began when 5 Ceriodaphnia were randomly selected and placed into each replicate of each sample by using a clean glass pipette. A recount was made to ensure that all chambers had five organisms. The test tray was placed back into the water bath-, covered with glass and the test initiation time of 11:45 am was recorded.

Chemistry

Water parameter analysis conducted on the effluent samples and control water included; alkalinity, ammonia, conductivity, dissolved oxygen, hardness, pH, and temperature. The methods used for all chemistry analysis were described in ASTM 14th edition. The ASTM method for

dissolved oxygen was used to calibrate a YSI model 54A DO meter. The ammonia analysis methods were taken from Orion Research Inc. owners manuals for the model 720 pH/ISE meter and electrodes for ammonia. Residual chlorine was not measured. The remaining unused sample portions were stored at 4°C.

Results

All observations are documented on the following data sheets. Sample #1 began to show signs of toxicity to the Ceriodaphnia at 12:45 pm, they appeared very lethargic. A dissecting scope provided the capability to detect the slightest activity of the organisms appendages. Mortalities began occurring in sample #1 within two (2) hours from test initiation. All Ceriodaphnia in sample #1 died 3 hours and 56 minutes later, 3:41 pm. Final pH and DO was measured upon termination of the sample #1 test.

All Ceriodaphnia in sample #2 and moderately hard control survived the entire 48 hours. After 24 hours, a few Ceriodaphnia in sample #2 displayed lethargic behavior, however they did survive the length of the test. The control and sample #2 were renewed with fresh solution at 11:50 am 4/15/92. The tests were terminated at 11:45 am on 4/16/92. Final pH and DO was measured on the remaining samples.

The results of sample #2 test indicate no acute toxicity. However, to determine any toxicity in sample #2, a chronic toxicity test with serial dilutions could be conducted. Thank you for your service and please contact us if any further testing is desired.

All Christensen

Allan M. Christensen
Aquatic Toxicologist

References

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Environmental and Analytical Services

January 24, 1992
Project 5000-286

Mr. Ron Klinker
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Hennepin Paper Company
P.O. Box 90
Little Falls, Minnesota 56345

Dear Ron:

Attached are the toxicity results from the hydrogen peroxide and chlorine dioxide spiked effluent samples. Ceriodaphnia dubia time-to-lethality data were again used to assess effluent toxicity.

Hydrogen peroxide treatment of the effluent caused no appreciable decrease in effluent toxicity; 100% mortality occurred in all treatments within two hours of test initiation. Chlorine dioxide treatment of the effluent also did not result in improved organism survival; complete mortality occurred within six hours (100% effluent treatments) and twenty-four hours (50% effluent treatments) of test initiation in the blank and ClO₂ effluent treatments.

Significantly increased survival was observed in effluent treated with powered activated carbon (PAC). Improved survival after this treatment generally implicates an organic compound as the toxicant, but this treatment -is not extremely selective and does not lend itself to any more specific classification of the toxicant. Subsequent investigation into wastewater treatment alternatives or toxicant identification should utilize the PAC information as a starting base.

Please contact me to discuss these options in greater detail.

Sincerely yours,

George Buttke
Biologist
Aquatic Biology Group

Attachment

Survival data for Ceriodaphnia dubia Time-to-Lethality tests, Hennepin Paper Co., Little Falls, Minnesota, IPS Project 5000-286.

Nov. 27, 1991

Elapsed Time	Control	Percent Survival					
		Blank Effl.		20 ppm H ₂ O ₂		100 ppm H ₂ O ₂	
		50%	100%	50%	100%	50%	100%
10 min.	100	100	100	100	100	100	100
20	100	100	100	100	100	100	100
40	100	100	30	100	70	100	80
60	100	100	0	80	50	100	10
2 hr.	100	0		0	0	0	0

Dec. 18, 1991

Elapsed Time	Control	Percent Survival							
		Blank Effl.		PAC Effl.		2 ppm ClO ₂		25 ppm ClO ₂	
		50%	100%	50%	100%	50%	100%	50%	100%
10 min.	100	100	100	100	100	100	100	100	100
20	100	100	100	100	100	100	100	100	100
40	100	100	100	100	100	100	100	100	100
60	100	100	100	100	100	100	100	100	100
2 hr.	100	100	60	100	100	100	60	100	50
3	100	100	60	100	100	100	60	100	30
4	100	100	50	100	100	90	60	70	0
6	100	80	0	100	100	80	0	0	
24	100	0		90	0	0			
48	100			70					

Residual chlorine was detected in the 25 ppm ClO₂ sample after test initiation. A sample which had undergone dechlorination with sodium thiosulfate still exhibited 100% mortality within 24 hours.

APPENDIX 4

PROCESS CONTROL DESCRIPTION

FINAL WASTEWATER TREATMENT SYSTEM
HENNEPIN PAPER COMPANY
LITTLE FALLS, MN

The final Wastewater Treatment System for the Hennepin Paper Company consists of a Parkson DynaSand Filter in series with a Calgon Model 4 Carbon Filter. The specific process is as follows:

The plant process water is currently being treated by an activated sludge treatment system. As the system currently operates, during peak usage periods, the system overflows to the Mississippi River. The goal of the new system is to reduce, or completely eliminate the amount of water discharged to the river. The New Final Treatment System will be tapped into the existing system below the Surge Tank and will provide a continuous flow of 120 GPM to the DynaSand Filter. Level will be monitored in the Surge Tank by Level Transmitter "LT-3". LT-3 will transmit a 4-20 MADC output signal proportional to level to the Supervisory Control Panel where it will be displayed. The start and stop setpoints for the DynaSand Feed Pump will be dependent on the level in the Surge Tank. These setpoints can be entered by the operator through a programming keypad located on the Supervisory Control Panel. If the level in the Surge Tank rises above the operator entered "High Level" setpoint, an alarm will be annunciated and an exterior alarm light will be activated. If the level in the Surge Tank drops below an operator entered setpoint, the Supervisory Control panel will "lock out" the DynaSand Feed Pump.

A 4-position, On-Off-Auto-Remote switch, is located on the door of the supervisory panel for control of the DynaSand Feed Pump in either manual or automatic mode. A remote Hand-Off-Auto switch is also provided at the pump which will allow the operator to manually operate the pump with the supervisory mounted HOAR switch in the remote position. With the supervisory mounted switch in the auto position (and the remote mounted switch in the auto position), the pumps will operate based on

operator entered setpoints corresponding to the surge tank and effluent sump levels. In the hand mode the operator can manually turn the pump on and off from the supervisory control panel (as long as the remote mounted switch is in the auto position). If the DynaSand Feed Pump is required and after a time delay the supervisory control panel does not receive a run signal, a pump failure will be annunciated at the supervisory panel. This failure will be acknowledged when the problem is resolved.

The DynaSand Feed Pump is also equipped with a local disconnect switch at the pump. This switch has an auxiliary contact which is input into the PLC for monitoring. If the DynaSand Feed Pump is required and the disconnect switch is open, A DynaSand Feed Pump Failure will be annunciated and the programming keypad will indicate that it is due to the disconnect switch being open. Once the switch is closed, the failure alarm will be discontinued.

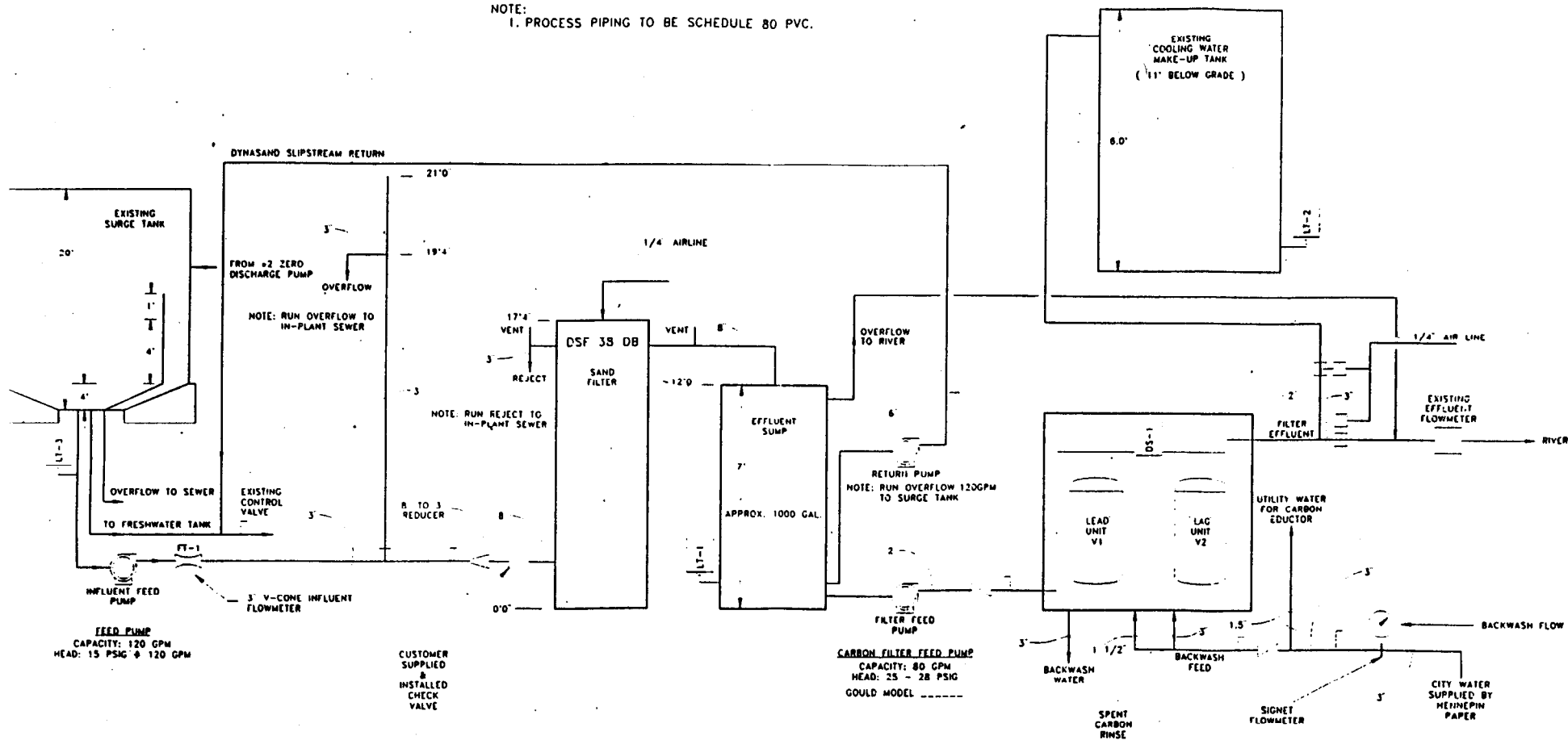
The influent flow to the DynaSand will be monitored by Influent Flowmeter FT-1. This flow will be displayed and recorded on a two pen chart recorder on the Supervisory Control Panel. The second pen of the chart recorder will be available for use in displaying the Effluent Flow. It will be capable of accepting a 4-20 MADC input signal from the existing Effluent Flowmeter (provided by Hennepin Paper).

The process flow will be pumped through the DynaSand Filter and into the "Effluent Sump". During normal operating conditions, the operating differential pressure across the DynaSand Filter is between 16" and 18" of water column. There will be an overflow riser pipe which will not allow the differential pressure across the DynaSand to exceed 24". The reject water from the DynaSand will be directed back to the sewer for injection back into the system.

The level of the Effluent Sump will be monitored by Level Transducer "LT-1". LT-1 will transmit a 4-20 MADC signal proportional to Effluent Sump Level to the Supervisory Control Panel where it will be displayed.

A "Slip Stream" will be continuously pumped from the Effluent Sump back to the Surge Tank by the Slip Stream Return Pump. The Slip Stream Pump and the DynaSand Feed pump are the same size and theoretically should pump at the same rate. A 3-position, Hand-Off-Automatic switch, is

NOTE:
1. PROCESS PIPING TO BE SCHEDULE 80 PVC.




FEED PUMP
CAPACITY: 120 GPM
HEAD: 15 PSIG @ 120 GPM

CUSTOMER
SUPPLIED
&
INSTALLED
CHECK
VALVE

CARBON FILTER FEED PUMP
CAPACITY: 80 GPM
HEAD: 25 - 28 PSIG
GOULD MODEL

- NOTES:
1. START FILTER FEED PUMP WHEN WATER LEVEL IS 1 FOOT BELOW TOP OF OVERFLOW STANDPIPE.
 2. LOCKOUT LEVEL FOR INFLUENT FEED PUMP WILL BE 5 FEET BELOW TOP OF OVERFLOW STANDPIPE.
 3. SLIP STREAM FROM THE DYNASAND MUST BE RETURNED TO THE SURGE TANK.

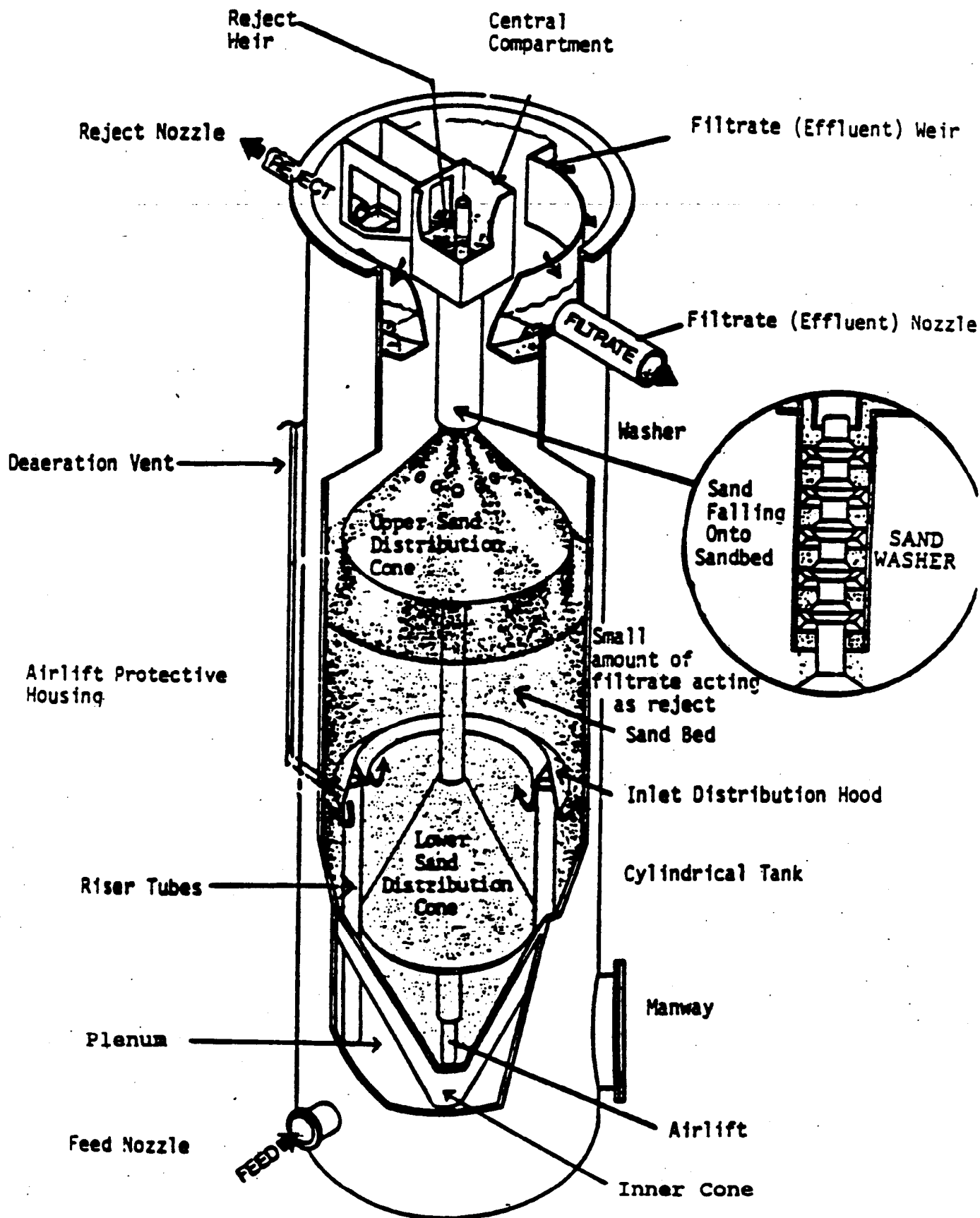
HYDRAULIC OVERVIEW

 AUTOMATIC SYSTEMS CO. P.O. BOX 120550 ST. PAUL, MN 55112		TITLE HYDRAULIC SCHEMATIC DIAGRAM	
CUSTOMER HENNEPIN PAPER, LITTLE FALLS, MN			
DRAWN JDL FILE HN_PAP_2'DWG 020924		SHT 10.	
SYM	REVISION	CHKD DL DATE '0-01-92	NO. DLJC-2

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THE PARKSON DYNASAND® FILTER
CYLINDRICAL TANK UNIT

Figure 1





MODEL 4

Granular Activated Carbon Adsorption System

The Calgon Carbon Model 4 is an adsorption system designed specifically for the removal of dissolved organic contaminants from liquids using granular activated carbon. The Model 4 reflects Calgon Carbon's extensive experience in adsorption system design and operation.

The Model 4 system is delivered completely assembled on a steel skid, requiring only site process and utility hookups to be ready for operation. The pre-engineered Model 4 design is available with three piping materials of construction options to satisfy most requirements.

The process piping network for the Model 4 accommodates operation of the adsorbers in parallel or series. In series operation, the first stage can be isolated from the flow, have the granular carbon exchanged, and returned to operation as the second stage without interrupting treatment.

The Model 4 system allows for ease of granular activated carbon exchange. The system is suited for use with Calgon Carbon's Bulk-Back Service in which the granular activated carbon is supplied in containers for convenient transfer to the adsorbers. Bulk-Back units also receive the spent carbon from the adsorbers for return to Calgon Carbon for reactivation services.

MATERIALS OF CONSTRUCTION

Adsorbers: Carbon steel ASME code pressure vessels
Adsorber internal lining: Vinyl ester lining (nominal 40 mil)
for potable water and most liquid applications

System external coating: Epoxy mastic paint system

Standard adsorption system piping options:

Solid PVC Piping System

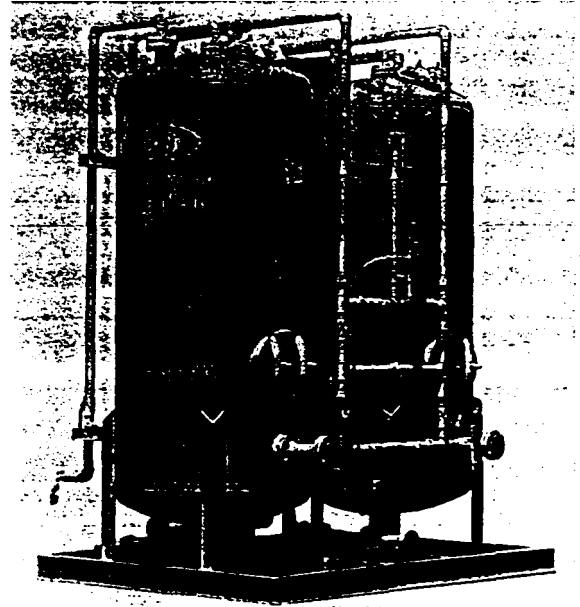
- Schedule 80 PVC pipe and PVC ball valves
- Schedule 80 PVC underdrain and PPL screened nozzles

Carbon Steel Piping System

- Schedule 80 steel pipe and ductile iron ball valves
- PPL lined carbon discharge with TFE lined plug valve
- Schedule 80 PVC underdrain and PPL screened nozzles

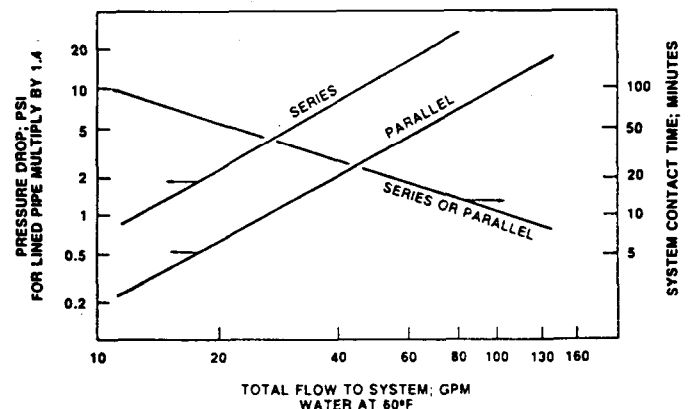
Polypropylene Lined Piping System

- PPL lined steel pipe and diaphragm valves
- TFE lined plug valves on carbon fill and discharge
- Solid PPL underdrain and screened nozzles



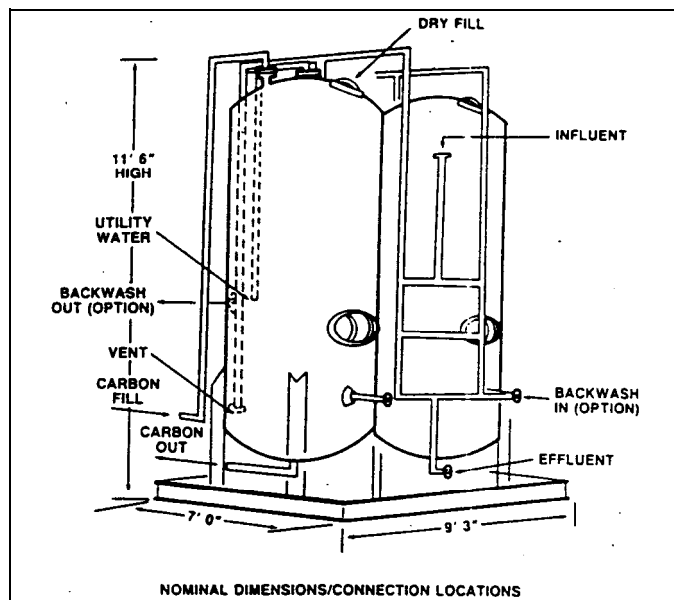
OPERATING CONDITIONS

Carbon per adsorber:	72 cubic feet (2,000 lbs)
Pressure rating:	75 psig
Pressure relief:	Rupture disk - 72 psig setting
Vacuum rating:	14 psig
Temperature rating:	150°F maximum
Backwash rate:	125 gpm (40% expansion)
Carbon transfer mode:	Pressure slurry transfer
Utility air:	30 scfm at 30 psig (not recommended for PVC pipe)
Utility water:	100 gpm at 30 psig
Freeze protection:	None provided; enclosure or protection recommended



DIMENSIONS AND FIELD CONNECTIONS

Adsorber vessel diameter:	4 ft
Process pipe:	2 in
Process pipe connection:	2 in flange
Utility water connection:	1 1/2 in flange
Utility air connection:	3/4 in hose connection
Carbon hose connection:	2 in Kamlok type
Carbon dry fill opening:	top 11 in x 15 in handhole
Backwash connections:	3 in flange
Drain/vent connection:	2 in flange; unrestricted
Adsorber maintenance access:	14 in x 18 in manway
System shipping weight:	9,000 lb with carbon
System operating weight:	26,000 lb



CAUTION

Wet activated carbon preferentially removes oxygen from air. In closed or partially closed containers and vessels, oxygen depletion may reach hazardous levels. If workers are to enter a vessel containing carbon, appropriate sampling and work procedures for potentially low-oxygen spaces should be followed, including all applicable federal and state requirements.

For more information on the product described in this bulletin, or information on other adsorption equipment, please contact one of our Regional Sales Offices located nearest to you:

SALES OFFICES

Region I
 P.O. Box 6768
 Bridgewater NJ 08807
 Tel(908)526-4646
 Fax (908) 526-2467

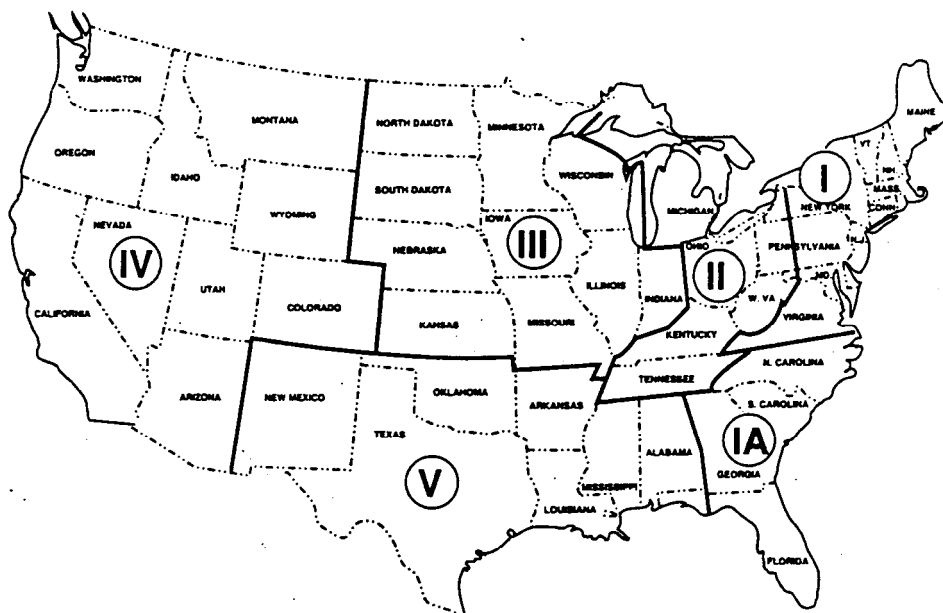
Region IA
 5600 77 Center Drive
 Suite 200
 Charlotte NC 28217
 Tel(704)527-7580
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Region II
 P.O. Box 717
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 Fax (708)505-1936

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 San Mateo CA 94403
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 Fax (415)574-4466

Region V
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 Tel (713) 690-2000
 Fax (713) 690-7909

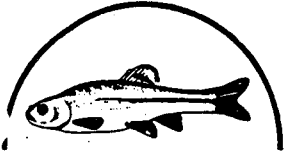


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 Boite 7
 B-1200 Brussels, Belgium
 Tel3227730211
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APPENDIX 5



Environmental Monitoring Inc.

P.O. Box 665, New Ulm, MN 56073-0665

Phone (507)359-1277

Results of a 48 hour Acute Toxicity Test for Hennepin Paper Co., Little Falls, MN.

An acute toxicity test was conducted for the Hennepin Paper Company beginning March 16 and terminating March 18, 1993. This test compared results between whole and filtered effluent. These two (2) effluent samples were collected on March 15, 1993 using the grab sample method. The collection and measurement of the pH and temperature was performed by Mr. Ron Klinker of Hennepin Paper. After collection, each sample was poured into respective cubitainers, placed into a shipping cooler, covered with ice and sent via Federal Express. The samples arrived March 16, 1993 at 11:30 am. Upon arrival, the temperature of the samples were recorded and pre-test procedures began.

TEST ORGANISMS & TEST PROCEDURES

The Ceriodaphnia dubia are raised in hard reconstituted water and are from in-house cultures. Transferring the adult Ceriodaphnia into a fresh medium one day prior to testing provided less than 24 hour old neonates. These neonates were collected and placed into a 1 liter beaker containing hard reconstituted water.

Reference toxicity testing was performed March 10, which provided data on the healthy condition of the test organisms. See Table 1.

Table 1. Reference Toxicity Test LC50 Value for March 93.

	LC50 g/L NaCl
Ceriodaphnia dubia	2.12

These results are consistent with our control charts.

Both effluents and the hard reconstituted water control used four (4) replicates during the test. Fifteen (15) milliliters of each solution was poured into thirty (30) ml polystyrene cups (test chambers). The test chambers were placed into a 25°C recirculating water bath and allowed to acclimate. When a stable temperature was reached, initial chemistry parameters were recorded. The test began when five (5) Ceriodaphnia were randomly selected and placed into each replicate of each sample by using a clean glass pipette. A recount was made to ensure that all chambers had five organisms. The test tray was placed back into the water bath, covered with glass and the test initiation time of 1:15 pm was recorded.

CHEMISTRY

Water parameter analysis was conducted on the effluent samples and control water. See Table 2.

Table 2. Initial Chemistry Measurements.

Whole Effluent	
Hardness	764.4 mg/L
Alkalinity	188.9 mg/L CaCO ₃
pH	7.56
DO	8.1 mg/L
NH ₃	0.569 ppm as N
Conductivity	4370 uS/m
Filtered Effluent	
Hardness	667.4 mg/L
Alkalinity	195.3 mg/L CaCO ₃
pH	7.58
DO	8.9 mg/L
NH ₃	0.992 ppm as N
Conductivity	3810 uS/m
Control	
Hardness	162.9 mg/L
Alkalinity	109.1 mg/L CaCO ₃
pH	8.46
DO	8.1 mg/L
NH ₃	0.001 ppm as N
Conductivity	537 uS/m

The methods used for all chemistry analysis are described in APHA 14th edition. The APHA method for dissolved oxygen was used to calibrate a YSI model 54A DO meter. The ammonia analysis methods were taken from Orion Research Inc. owners manuals for the model 720 pH/ISE meter and electrodes for ammonia. Residual chlorine was not measured. The remaining unused sample portions were stored at 4°C.

RESULTS

Whole Effluent killed 13 out of the 20 Ceriodaphnia involved in the test. No mortalities were observed in the filtered effluent or control samples.

Conducted by:

Al Christensen

Approved by:

Michael J. Jansen

REFERENCES

USEPA, EPA/600/4-85/013, Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms.

USEPA, EPA/600/4-89/001, Short term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms.

APHA, Standard Methods for the Examination of Water and Wastewater 1985 14th Ed. American Public Health Association, Washington, D.C.