

PASSIVE NUTRIENT ADDITION
FOR THE BIODEGRADATION
OF ETHYLENE GLYCOL
IN STORMWATER

Thesis

Submitted to

The School of Engineering at the

UNIVERSITY OF DAYTON

In Partial Fulfillment of the Requirements for

The Degree

Masters of Science in Civil Engineering

by

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UNIVERSITY OF DAYTON

Dayton, Ohio

December 1998

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PASSIVE NUTRIENT ADDITION FOR THE BIODEGRADATION OF ETHYLENE
GLYCOL IN STORMWATER

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ABSTRACT

PASSIVE NUTRIENT ADDITION FOR THE BIODEGRADATION OF ETHYLENE GLYCOL IN STORMWATER

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The purpose of this research is to study the effect of the passive addition of a solid form, slow-release, nutrient source on the the microbiological degradation of carbonaceous pollutants. Ethylene glycol (EG) was used as a model pollutant in the research. The design and experimental operation of the microbiological contactors is a proof of concept study.

Studies were performed on three microbiological contactors operating in parallel. All three contactors were physically identical and operated under identical conditions. One contactor served as a control and had no nutrient source added while the other two had a solid form, slow-release nutrient source added. The low level nutrient source contactor initially had 100 grams of Sta-Green[®] fertilizer and the high level nutrient source contactor had 150 grams of the same fertilizer.

A comparison between the data collected from a contactor with dissolved nutrients added in the feed (idealized conditions) and the data from the high level nutrient source contactor was performed. The high level nutrient source contactor rendered similar or better results than the contactor system with nutrients dissolved in the feed (idealized). The comparison of the data for the two contactors indicated that both contactor effluent concentrations of EG were between 25 mg/L and the detection limit of 5 mg/L.

The control contactor achieved approximately 15% to 30% EG removal. The low level nutrient source contactor was inconsistent, for various reasons discussed below, but could achieve EG removals in the 50% or better range, while the high level nutrient source contactor typically achieved 75% to 100% EG removal efficiencies.

Moreover, a comparison of nutrient influent and effluent, and a theoretical nutrient demand based on a C:N:P ratio (100:5:1) was also performed. The higher than theoretical C:N ratio obtained from the contactors indicate the possibility of the presence of a secondary nitrogen source in the contactor.

An additional study was conducted to evaluate the recuperation process of the contactors under intermittent flow conditions and to verify that the inoculated bacteria would remain active due to the presence of a moisture retaining additive, Soil-Moist. This study included shutting down the low nutrient contactor for 194 hours and then turning it back on. The EG concentration level briefly rose to 140 mg/L but decreased to 11 mg/L (pre-shut-down conditions) within 96 hours. This indicates a healthy microbial

population and the presence of sufficient moisture due to the Soil-Moist additive to keep the population active during non-flow conditions.

After operating the contactors for over 2,200 hours, it was concluded that the passive addition of a solid form, slow-release, nutrient source was as effective as if the nutrients had been added in its soluble form. Among the 3 contactors studied, the high level nutrient source contactor exhibited the best aerobic microbiological degradation properties indicated by the high percent removal values of EG.

In addition, data collected for nitrate and total nitrogen tests were below detection limit. The very low levels of nitrate indicated that the aerobic nitrification and anaerobic denitrification processes might have occurred.

ACKNOWLEDGMENTS

My special thanks are in order to Dr. Steven Safferman, my advisor, for providing the time, effort, equipment, and personnel necessary for the work contained herein, and for directing this thesis and bringing it to its conclusion with patience and expertise.

I would also like to express my appreciation to Jennifer Thomas, who offered assistance in running the physical aspect of the project and helped maintain a well organized and detailed log book. Jen, without your help, this research would have put to an end any of my hopes of having a “personal life.”

Thanks also need to go out to Stephanie Sigler, the part-time bartender who would occasionally make us wonder where the missing EG went. Steph, thank you for taming that crazy Gas Chromatograph and putting all the extra time and effort into this research.

I also want to thank Izumi Nakaya for her help with data analysis and compilation and for being such a great source of knowledge. Did anyone know that Samurais do not really exist in Japan or anywhere else? Thanks for the clarification and the help Izumi.

Thanks are also in order to Dr. Donald Chase for his time and effort to being on my committee. Sorry Doc. I couldn't find anyone else to torture.

Thank you to Dr. Joseph Swartzbaugh for taking personal time on his week-end to explain to me a few things about writing a Masters Thesis and for his time and effort to be on my committee. Doc, you will always be remembered as Pops.

And last but not least, thanks to my girlfriend, Erin, who has been very patient and understanding throughout this entire research.

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LIST OF SYMBOLS / ABBREVIATIONS

Deicing – Spraying or spreading of anti-icing fluids, such as ethylene glycol, on aircraft and runways to remove or stop ice from forming.

Aerobic – Growth in the presence of molecular oxygen (usually air).

PG – Propylene glycol.

Microorganisms – Microscopic organisms that exist naturally in the environment or are added as an inoculum.

Contactors – A unit that supports a microbial biofilm and allows the contact of microorganisms with contaminated stormwater.

EG - Ethylene Glycol, an alcohol used in deicing fluids; $C_2H_6O_2$; See Figure 1-1 below for structural formula.

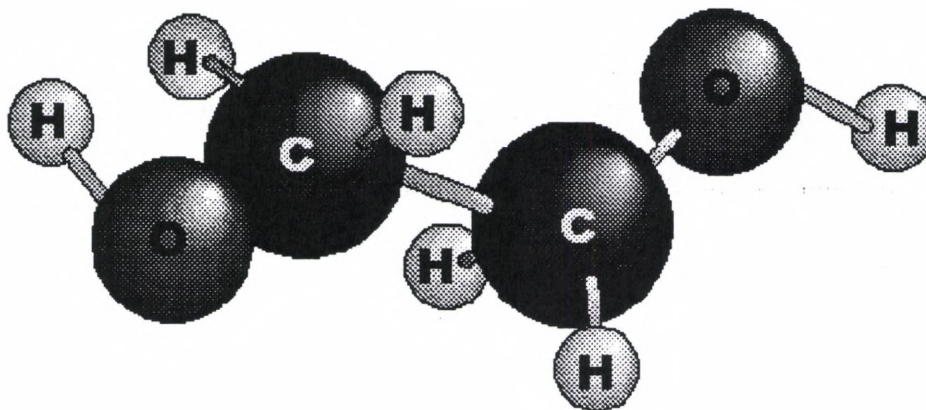


FIGURE 1.1 – Structural Formula of EG

DI water – de-ionized water

DF - de-icing fluid/s.

O&M - Operation and Maintenance

EPA - Environmental Protection Agency

Biochemical Oxygen Demand (BOD) – The amount of molecular oxygen utilized by microorganisms for the degradation of organic material.

Biodegradation – The breakdown process of organics by microorganisms.

TRI – Toxic Release Inventory

CBOD – Carbonaceous BOD

$^{\circ}\text{C}$ – Degree Celcius

$\%$ - Percent

mg/m^3 – milligrams per cubic meter

ml - milliliters

$\$$ - Dollar/s

PVC – Poly Vinyl Chloride

rpm – revolutions per minute

TN – Total Nitrogen

DO – Dissolved Oxygen

GC – Gas Chromatograph

KCI – Kansas City International

CHAPTER I

INTRODUCTION

Overview

This research was conducted as a proof of concept study to analyze the potential of the passive addition of a solid form, slow-release, nutrient source to allow the aerobic microbiological degradation of ethylene glycol polluted storm water in a subsurface microbiological contactor. The findings, however, may be applicable to other predominantly carbon-polluted stormwater. Based on the literature search conducted, the approach of utilizing the passive addition of a solid form, slow-release, nutrient source has not been attempted before.

A specific pollutant, ethylene glycol (EG), was the focus of the study. EG is used in numerous applications but the main interest in this research is its presence in stormwater runoff from aircraft deicing fluids. Deicing fluids (DF) are used worldwide in considerable quantities as a mean to remove snow, frost, and ice from aircraft (Johnson, L., 1997). An estimated 3785 liters of DF are needed to deice a large passenger plane (Aviation Week and Space Technology, 1991). EG has a very low freezing point -13°C for pure liquid, and a temperature in aqueous solution of -50°C (US Department of Transportation, 1991), and thus, is an excellent antifreeze liquid. In very cold weather,

aircraft pilots often find themselves, passengers, and their planes unable to proceed with the flight because of freezing rain and snow that forms a thin coat of ice on the wings, reducing the lift by as much as half. EG is sprayed onto the wings of aircraft to melt ice and/or prevent its formation. In most cases, the freezing point of the EG and water mix is lower than the ambient air temperature, therefore allowing aircraft to function under freezing weather conditions. The most common form of DF is EG and propylene glycol (PG). These glycol compounds are readily mineralized by microorganisms to carbon dioxide and water. DFs are also occasionally used to keep runways and taxiways accessible.

It is estimated that eighty five percent of all applied DF end up being deposited on the ground (ATSDR, 1996). In major airports, most of the DF deposited on the ground is collected at the point of application; however, a considerable amount, fifteen percent, still finds its way to storm sewers, retention ponds, and streams due to deposition after aircraft takeoff.

EG and PG exert a high microbial oxygen demand that renders them a problem to the environment. The 5-day Biochemical Oxygen Demand (BOD₅) at 20°C for pure EG has been reported to be in the range of 400,000 to 800,000 mg/L (Halterman-O'Malley, A., 1997). The Carbonaceous BOD (CBOD) required by diluted DF is equivalent to the daily requirements of CBOD by domestic wastewater generated by 5000 people (Johnson, L., 1997). The high oxygen demand depletes the dissolved oxygen (DO) in ponds, lakes, rivers, and streams killing the fish and other oxygen demanding species.

Many of the airports in the United States are regulated by the Environmental Protection Agency (EPA) and have taken measures to collect these fluids at the point of application. Airports may send the collected deicing fluids to wastewater treatment plants, to recycling units, and/or release it directly to receiving streams if the concentration is low enough to do so. The problem with recycling DFs is that a high enough initial concentration is needed in order to make it economically feasible. Most wastewater treatment facilities will require the glycol fluids to be diluted to less than 10 percent before they are accepted due to the high BOD requirements (Johnson, L., 1997). Some wastewater treatment plants do not have the hydraulic capacity to accommodate the high flows of stormwater containing DF. The dilution and metering requirements imposed by the wastewater treatment facilities on airports create a storage problem of the stormwater and will require building additional detention structures at the airport to hold the stormwater.

Research Objective

Microbes in nature will degrade EG by using it as a food source and using dissolved oxygen as an electron acceptor. The purpose of this research is to study the effect of the passive addition of a solid form, slow-release, nutrient source on the the microbiological degradation of the carbonaceous pollutant EG. This research is designed to provide airports and others with an inexpensive tool that requires very minimal operation and maintenance (O&M) to biodegrade carbonaceous pollutants.

The microbiological contactor proposed for field use is proposed to be designed as a subsurface, static unit, requiring no moving parts or electric input. It will use a commercially available, solid form, slow-release, water soluble nutrient source to supply the required nutrients to the microbes biodegrading the DF in stormwater. The microbiological contactor will require minimal operation and maintenance in order to enable its use in remote areas where electric and access is not readily feasible. The microbiological contactor must be placed underground to maintain a temperature range at which microbes will remain active.

Like a trickling filter, the microbiological contactor will have a medium where microbes will attach to form a biofilm. The uniqueness of the microbiological contactor when compared to a trickling filter lies in two important differences. Unlike a trickling filter, the microbiological contactor can go without hydraulic loading for several days and still maintain a living biofilm. This feature is enhanced by adding a moisture additive that will retain water and supply the biofilm with the needed moisture during no flow conditions (R. Nath, 1997). Another difference between a trickling filter and the microbiological contactor is the solid form, slow-release nutrient source that the microbiological contactor provide.

Scope

This research is a continuation of studies conducted by Dr. Steven Safferman of the University of Dayton, as well as Rupak Nath and Azeez Saliba, both Masters program graduates from the University of Dayton.

The general experimental plan involved the construction and operation of three (3) microbiological contactors in a laboratory environment. All three contactors were packed with a rock media to which microbes attach and a moisture additive that maintains a fairly consistent moisture content throughout the contactor. The three independent contactors ran simultaneously.

The experiment was conducted in two phases. Phase I involved operating the contactors until equilibrium was achieved (defined as having the percent removal of ethylene glycol remain constant over 5 days). Phase II involved shutting down a contactor for a given period of time and documenting the recovery process and subsequently the efficiency of that contactor. This was achieved by comparing the contactor EG effluents before and after it was shut down.

To initiate Phase I, a leaching study was conducted on numerous commercially available fertilizers in order to choose a nutrient source for the contactors. Sta-Green[®] was selected as the fertilizer of choice due to its consistency in providing a slow-release source of nutrients with time. Concurrently with this source selection study, the contactors were started so that the biofilm could be developed. A nutrient level nomenclature was used to differentiate between the contactors. One of the contactors was run as a control and had no nutrient source added while the other two contactors included two levels of a solid form, slow-release, nutrient. The high nutrient level contactor had 150 grams of Sta-Green[®] fertilizer while the low nutrient level contactor had 100 grams of Sta-Green[®]. In

addition, a parallel nutrient leaching study was performed to compare the nutrient influent level going into each contactor and effluent levels coming out. The research was conducted mostly under continuous flow conditions, an ambient room temperature ranging from 20 °C to 25 °C, and a controlled pH range of 6 to 8.

The research was conducted over a period of four month to allow the bacterial colony to be established and the biological activity to stabilize. Samples of effluent from each contactor were taken on a daily basis for analysis. No attempt was made to identify the microorganisms in the contactors.

CHAPTER II LITERATURE REVIEW

Background

Deicing fluids from runoff at airfields, taxiways, and off aircraft have been found to contain high levels of EG while exhibiting low levels of nutrients. The high concentration of EG is polluting rivers, streams, and lakes due to the high oxygen demand required for EG biodegradation.

EG and PG are clear liquids that are used in antifreeze and deicing solutions. Exposure to large amounts of ethylene glycol can damage the kidneys, heart, and nervous system. Both compounds can change body chemistry by increasing the amount of acid. Exposure to the skin and lungs may cause irritation. Lethal quantities in adults are considered to be 100 ml of pure EG, but in children, much less may cause serious cardiac, renal, and CNS toxicity (Chemical Market Report, 1998). Peak blood levels are generally seen in 1-4 hours (Chemical Market Report, 1998)

EG is the most widely used of the commercially available aliphatic glycols (1,2-alkanediols). It is produced by the non-catalytic liquid-phase hydration of ethylene oxide. In January 1996, worldwide capacity was approximately 22.6 billion pounds (10.2

million metric tons) (Inspection report on FAA deicing program, 1996). In 1995, its production volumes ranked it among the top twenty organic chemicals in the United States. Most ethylene glycol goes into the production of polyester products (fibers, film, solid-state resins and other products), some food, medical and cosmetic products, antifreeze, and deicing fluids. Other smaller uses are in hydraulic fluids, surface coating, unsaturated polyester resin, and surfactant markets.

In 1996, releases of ethylene glycol were 18,568,505 pounds. Of those releases, 6,019,772 pounds were released into the air; 1,842,307 pounds into surface water, 429,976 pounds onto land, 1,842,307 pounds to underground injection, and 2,576,966 pounds hauled for disposal off-site (TRI, 1996). EG has been found in at least 34, and PG in at least 5, of the 1,416 National Priorities List sites identified by the Environmental Protection Agency (EPA) (ATSDR, 1996).

The United States Army has established a reduction goal for ethylene glycol disposal of 100%. The United States Air Force eliminated the use of EG from all its facilities in 1992 and replaced it with PG, a less toxic DF (Haltermann-O'Malley, A., 1997).

Biodegradation

Biodegradation rates are influenced by physical and chemical factors. These factors include the size of the microbial population, the availability of moisture (water), food (a carbon source), an electron acceptor (oxygen or other), macro nutrients (nitrogen and

phosphorus), micro nutrients (including trace amounts of Fe, K, Mg, Ca, Zn, Mo, Cu, and Mn), and the physical and chemical properties of the molecule being degraded.

In liquid, microbes are either suspended, as in an activated sludge processes, or attached to a medium. A fixed film is an active microbial colony that is attached to a media.

Media can be man-made such as plastics, cloth, composite materials, and metal structures, or natural such as rocks.

Factors Affecting Biodegradation

Microbial activity can be optimized under certain environmental conditions including temperature, pH, moisture, and electron acceptor availability. Microbial activity temperature ranges from 20°C to 70°C (K. Baker & D. Herson, 1994) and in general a 10°C increase in temperature will double the reaction rate. The biodegradation rate is also affected by the pH of the overall environment surrounding the microbes. The optimal pH for microbial activity is usually between 5.5 and 8.5. However, biodegradation can occur in extreme pH ranges due to the activity of some unique microorganisms which grow in very acidic or alkaline environments. Moisture plays an important role in the rate of biodegradation due to the importance of water for the transfer of substrates in the byproducts out of the cell. Fixed film microbes cannot move, so water acts as a transport mechanism of food to the cells. The presence of an electron acceptor is also vital for the growth of the microbial biofilm. The absence of an electron acceptor, oxygen in this case, will impede the growth of the bacteria, thus affecting the efficiency of the contactor system.

The structure and complexity of a compound will also determine its potential for degradation. Generally, hydrocarbons can degrade under aerobic conditions, with simple hydrocarbons being degraded faster than complex ones (Baker, K. And Herson, D., 1994). The bio-availability of contaminants is also very vital in the growth and health of a microbiological culture. Contaminants that are not water soluble may reside in soils or other media and thus not be available for microbial biodegradation. Carbon, nitrogen, and phosphorous are required for cell growth and biosynthesis of most microbial constituents.

Rules and Regulations

Ethylene glycol is regulated by the Food and Drug Administration as a residual in food. The American Conference of Governmental Industrial Hygienists (ACGIH) lists an adopted short term exposure limit value of 100 milligrams of ethylene glycol per cubic meter of air (100 mg/m³) for a 15-minute exposure (ACGIH Worldwide, 1998). The federal Clean Air Act of 1990 classified ethylene glycol as a hazardous air pollutant. The act requires users to carefully monitor the fluid's application and deposition, raising administrative and handling costs. Airlines that have relied on ethylene glycol as an aircraft deicing agent have been forced to re-evaluate its use. Neither EG or PG compound is likely to exist in large amounts in air since about half of the compounds that enter the air will break down in 24-50 hours.

EPA regulates EG as an air toxin on the Hazardous Air Pollutant List and as a volatile organic compound. It is regulated under the Clean Air Act, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and the Toxic Substances Control Act (ATSDR, 1996).

Under the Emergency Planning and Community Right-to-Know Act of 1986, annual releases of more than 5,000 pounds of ethylene glycol into the air, water, or land must be reported and entered into the national Toxic Release Inventory (TRI) (ATSDR, 1996).

Any time an airline uses ethylene glycol to keep ice off its planes, it must be reported. If more than 600 gallons are used collectively in any one day, the airport must report it to federal hazardous chemical monitors (The Spokesman-Review, 1998). The CERCLA regulations do not make use of ethylene glycol illegal, but appear to discourage its use.

Case Studies

The nation's 17 busiest airports annually release a combined 58 million pounds of ethylene glycol, a deicing agent that poses "significant" risks to human health (ATSDR, 1996). Until recently, thousands of gallons of ethylene glycol were used each winter to rid jets of snow and ice for safe takeoffs (Johnson, L., 1997). As an alternative, some airlines use nontoxic propylene glycol, but it costs as much as \$1 a gallon (Aviation Week and Space Technology, 1991).

Due to regulation imposed by regulatory agencies, primarily the EPA, on effluent concentrations of EG allowed to enter the nations waterways, airports have implemented different measures to deal with EG contaminated stormwater. Some airports use collection and detention ponds to hold the stormwater and eventually release it in controlled amounts into streams or to wastewater treatment plants, while others use treatments such as natural microbial activity in ponds or batch reactors. Some international airports have implemented a collection and recycling operation at the point of application. However, the above listed measures do not take into consideration the spilling of EG on the entire length of runways, but rather deal with collecting EG contaminated stormwater only at the point of application.

In Spokane and Seattle, it is illegal for car owners to intentionally spill antifreeze or dispose of it on the ground, but for years airlines have routinely spilled ethylene glycol on the ground while de-icing planes (The Spokesman-Review, 1998). At Spokane International, the chemical mixes with snow and rain runoff and is diverted to a storm ditch near the runways where it dissipates. Delta and United airlines have ethylene glycol available for de-icing while all other airlines at Spokane International use propylene glycol (The Spokesman-Review, 1998), which is less toxic than EG but remains as ecologically damaging as EG in terms of oxygen demand and its effects on surface waters.

Kansas City International (KCI) Airport is spending \$ 8.5 million to reduce the environmental hazards of deicing planes. Currently, the KCI wastes flow into lakes on

the airport property. In one of those lakes, the large Berlin Reservoir, a large dose of the deicing agent ethylene glycol killed fish in 1992. Ethylene glycol kills fish by consuming the oxygen in the water (The Kansas City Star, 1998).

Families who live along Mill Creek near the Dayton International Airport contend that chemicals used to deice runways and airplanes are flowing into the creek and have contaminated the groundwater, including several wells in the area (The Dayton Daily News, 1995). Dayton city officials contend that such deicing agents as ethylene glycol, propylene glycol, urea, and ammonia do not pose a health hazard (The Dayton Daily News, 1995). The city constructed a collection system at the point of application to capture the fluids and meter it to the local wastewater treatment plant.

At La Guardia airport, deicing operations are mostly conducted at the gates (passenger boarding area) rather than the deicing pads and the DF are not collected. In 1996, airport operator officials estimated that only one aircraft in the last two years used the deicing pad because air carriers are responsible for collecting glycols, and they do not use deicing pads if an aircraft can make it to the end of the runway within a few minutes of being deiced at the gate. (Inspection Report on FAA deicing Program, 1996)

Pittsburg International Airport has containment centers, collection ponds, for DF. The containment centers store and release DFs in controlled amounts to the wastewater treatment plants (Environmental Technology, 1997). In addition, Dulles International Airport in Washington D.C. has built containment structures where the DF is treated via

natural microbial activity and the effluent is released to waterways (Environmental Technology, 1997).

At Chicago's O'Hare International Airport, a drainage detention basin was constructed for the collection of DF contaminated stormwater runoff. The stormwater is then treated on-site biologically, using a sequencing batch reactor process.

Many other nationally large airports, such as Denver and Cincinnati, as well as other international airports have built collection systems for capturing point-of-application EG contaminated stormwater. International airports such as Munich, Oslo, and Lulea Airports employ a vast recycling operation of deicing fluids (Holmgren, A. And Forsling, W., 1993).

The subsurface microbiological contactor studied in this research is an additional viable option that could be presented to airports as an option for the biodegradation of EG in stormwater. This option could replace the need for batch reactors, recycling, and stormwater metering to wastewater treatment plants and/or the release into waterways. In addition, it will be proposed that the subsurface microbiological contactor be placed at the outfalls of the drainage areas surrounding the airport in order to catch the runoff from the point of application as well as the spills along miles of runway.

CHAPTER III PROCEDURES & EXPERIMENTAL DESIGN

This research is a continuation of previous research studies. This study was conducted to analyze the potential of the passive addition of a solid form, slow-release, nutrient source to allow the aerobic microbiological degradation of predominantly carbon-polluted stormwater in a subsurface microbiological contactor. The general experimental plan involved the construction and operation of three (3) microbiological contactors in a laboratory environment. All three contactors were physically identical, were packed with red volcanic rock media and an additive that maintains moisture during no flow conditions, and except for nutrient addition rates, were operated under identical conditions. The three contactors were run in parallel. The experiment was conducted in two phases. Phase I involved operating the contactors until equilibrium was achieved (as indicated by having the percent removal of EG remain constant over 5 days). Phase II involved shutting down a contactor for a period of seven days and monitoring its efficiency after restarting. This was determined by comparing the contactor EG effluents before and after it was shut down.

One of the contactors served as a control and had no nutrient source added. The other two had a solid form, slow-release nutrient source added. The low nutrient level

contactor initially had 100 grams of Sta-Green® fertilizer and the high nutrient level contactor had 150 grams of the same fertilizer.

Contactor Components

The fabrication materials used in building the microbiological contactors were commercially available from hardware stores and plumbing suppliers. The following sections detail each component of the contactor including the types and amount of materials used and how the contactors were assembled. Figure 3.1 presents a schematic of the system.

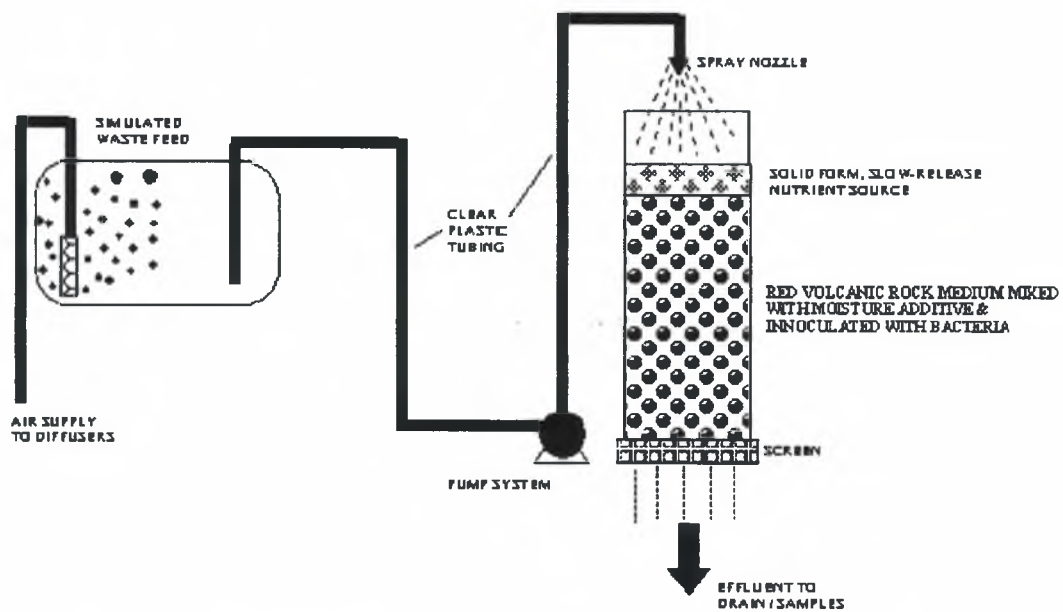


FIGURE 3.1 - SCHEMATIC OF MICROBIOLOGICAL SUBSURFACE CONTACTOR SYSTEM

Contactator Shell

The outer shell of the contactors was constructed from black, corrugated, PVC pipe. The pipe was seven inches in diameter and three feet long. The contactor pipes were mounted vertically onto a steel frame. A heavy construction-grade PVC mesh was placed at the bottom of the contactors pipes and fastened with a high density plastic fasteners. The purpose of the plastic mesh was to hold the contactor's media in place while still allowing drainage of fluids and the free flow of air through the contactor. The contactor unit is presented in figure 3.2.

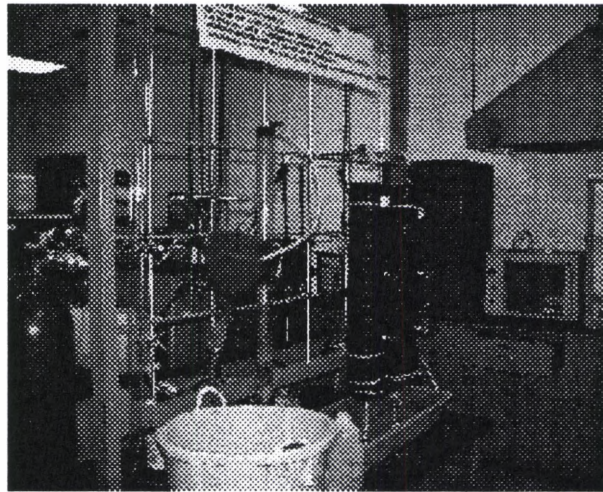


Figure 3.2 – Contactor Unit

Rock Medium

Five media choices studied were red volcanic rock, marble, granite, limestone, and sandstone. They were evaluated for external and internal porosity, water holding capacity, and tendency to dry.

The media of the contactors was red volcanic rock. Red volcanic rock was selected because of its water holding capacity (Saliba, A., 1997). Additional information on red

volcanic rock can be obtained from the Colorado Aggregate Company in Alamosa, Colorado.

The red volcanic rock was sized by passing it through a sieve. The rock that passed the 1-inch sieve but were retained on a subsequent ¾-inch sieve were selected for the reactor media. Following the size selection, the red volcanic rock was hand washed by placing it on a strainer with running tap water until the effluent water was clear. No detergents were used in the washing process. This step was intended to remove small rock particles and dust that was attached to the media pores. The rocks were placed in bowls in an oven at 103°C and allowed to dry overnight. After oven drying, the rocks were removed, covered, and placed in the laboratory for one and a half weeks to air dry.

Upon completion of the system set-up, 8,190 grams of the red volcanic rock media was placed in each contactor.

Moisture Additive

Three types of moisture retaining materials were evaluated; Soil Moist™, vermiculite, and regular sponge. The materials were evaluated to determine their water retention capacity and tendency to dry.

Moisture is essential in the development and survival of microbes. In order to maintain a moist environment in the contactors during no flow conditions, a moisture retaining material was included in addition to the media in the contactors. The selection of Soil

Moist™, the moisture retaining material, was based on the fact that it exhibits maximum water retention and slow rate of moisture release with time (Nath, R., 1997). To maintain the necessary required moisture during no flow conditions, 11.4 grams of Soil Moist™ was hydrated and applied to the rock media.

Soil Moist™ is a synthetic acrylic polyacrylamide with a potassium salt base. Initial soaking of the Soil Moist™ was required to prevent the polymer from going through the media. The pH of Soil Moist™ in an aqueous system is approximately 6.2 – 7.0. Soil Moist™ will absorb over two hundred times its weight in water (Soil Moist™ Polymers, 1996). Additional information on Soil Moist™ may be obtained from JRM Chemical, Inc.

Bacteria

In addition to the red volcanic rock media and the Soil Moist™, a colony of hydrocarbon feeding microbes was necessary to degrade contaminants. The microbes selected were MP Super CEE, Lot # 2096022, supplied by Microbe Masters.

Five (5) grams of the freeze dried bacteria were mixed with 1.5 liters of deionized water in a beaker and gently agitated on a shaker table. The rock media was submerged in the bacteria solution for approximately five minutes.

Pump and Tubing System

Three pumps equipped with a motor controller, to control the flow rate through each contactor, were used in this experiment. The motor controllers were connected to a timer. Each pump was connected to clear plastic tubing that conveyed the system feed to the spray nozzles. Metal clamps were used as weights for the clear tubing in the feed container in order to prevent the tubes from floating to the surface.

The MasterFlex pumps are model number 7553-70 and are adjustable from 6 – 600 revolutions per minute (rpm) and were obtained from Cole-Parmer Instrument Company. The motor controllers are also obtained from Cole-Parmer Instrument Company and are MasterFlex model number 7553-71. The timer is a Thomas Co. Lab. Controller S/N # 1073179 and was obtained from Control Company.

The flow rates to the contactors were set to 35 milliliters per minute (ml/min) using the fill and spill method. To maintain the overall average flow rate of 17.5 ml/min., the pump controllers were configured to operate intermittently 30 seconds on and 30 seconds off. For every 30 seconds the pumps were on, the spray nozzles delivered 35 ml of feed solution to each contactor.

Air was supplied via plastic tubing from a laboratory air supply faucet. The air passed through a filter, in order to insure cleanliness, and was supplied to the feed container by air difusers.

Spray Nozzles

A spray nozzle was connected to the clear plastic tubing from the effluent side of the pump. The spray nozzles are the plastic ends of the commercially available spray bottle. The purpose of the spray nozzles was to distribute the feed over the entire top surface area of the contactor, rather than point feed.

Feed Containers

The feed container was a 30-gallon bucket that is commercially available from a hardware or farm supply store. The pump and tubing system and feed container are presented below in figure 3.3.

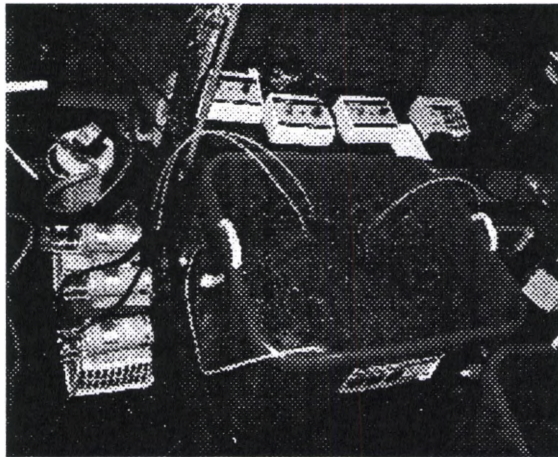


Figure 3.3 - Pump and Tubing System and Feed Container

Feed Components

Table 3-1 lists the chemical components used in preparing the feed source. The amounts shown are calculated to prepare 24 gallons of feed. Sodium hydroxide was used, on an as needed basis, to adjust the pH of the feed to 7.

Table 3-1 Chemical Components

Number	Parameter	Unit	Amount
1	Ethylene Glycol	ml	16.5
2	Ferric Chloride (FeCl ₃)	gm	0.099
3	Manganese Chloride (MnCl ₂)	gm	0.024
4	Zinc Sulfate (Zn SO ₄)	gm	0.071
5	Cupric Chloride (CuCl ₂)	gm	0.011
6	Cobalt Chloride (CoCl ₂)	gm	0.015
7	Ammonium Molybdate ((NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O)	gm	0.011
8	Sodium Borate (Na ₂ B ₄ O ₇ ·10H ₂ O)	gm	0.007
9	Calcium Chloride (CaCl ₂)	gm	0.679
10	Magnesium Chloride (MgCl ₂ ·6H ₂ O)	gm	1.245
11	Potassium Chloride (KCl)	gm	3.306
12	Sodium Citrate (Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O)	gm	0.899
13	Sodium Hydroxide (NaOH)	gm	As Needed
14	Yeast Extract	gm	0.006

Nutrient Source Component

The following commercially available fertilizers were considered as nutrient sources to be utilized in this experiment.

1. Jobe's 13-4-5 Plant Food Spikes
2. Jobe's 15-7-6 Tree Spikes
3. Aquarium Pharmaceuticals, Inc.'s 20-10-5 Pond Care Aquatic Plant Food
4. Scotts 31-3-9 polymer-encapsulated nitrogen lawn food
5. Scotts 18-6-12 Osmocote
6. Pursell's 18-6-12 time-released Sta-Green[®]

To determine the best nutrient for use in the contactors, the following preliminary studies were conducted. A sample of Jobe's Plant Food Spikes was added to the low nutrient level and high nutrient level contactors and run for 20 days. After 20 days, Jobe's Plant Food Spikes were removed from the contactors because of the rapid deterioration of the nutrient source and the inconsistency in the amount of nutrients leaching. The plant food spikes were replaced by Jobe's Tree Spikes as a nutrient source. The tree spikes lasted longer than the plant food spikes, however they were replaced by Sta-Green® time-release nutrients after 28 days. The Jobe's Tree Spikes also showed inconsistency of nutrient leaching as well as rapid deterioration.

During the 48 day time period between starting the reactors and the addition of Sta-Green® a parallel leaching study was being conducted to determine the fertilizer source that would maintain its physical integrity under direct hydraulic loading, and would provide a consistent leaching characteristic.

After testing the nutrient leaching characteristics of each of the listed fertilizers, Sta-Green® by Pursell's was selected as the fertilizer of choice due to its consistency of nutrient release. Additional information about Sta-Green® can be obtained from Pursell's Industries, Inc.

Measuring Equipments and Methods

Table 3-2 describes the laboratory equipment used and table 3-3 includes the analytical methods used for measurements throughout this research.

Samples were generally collected and analyzed daily from the effluent of each contactor to be analyzed for ammonia, chemical oxygen demand (COD), nitrate, total nitrogen (TN), phosphate, dissolved oxygen (DO), pH, temperature, and EG concentration. The samples used in the Gas Chromatograph (GC) were preserved with phosphoric acid, and the samples designated for COD, nitrate, TN, and phosphate were preserved with sulfuric acid. These samples were analyzed weekly. The samples obtained for DO, pH, temperature and ammonia were unpreserved since these parameters were to be measured immediately.

Ammonia present in the fertilizer is the primary source of nitrogen for the microbes in the contactors. Samples are collected daily and the concentration levels of ammonia is used as an indicator of the amount of nitrogen being delivered into the contactors. An increase or decrease in ammonia concentrations usually indicate an increase or decrease in nitrogen supplied to the microbes.

Although not essential for this research, due to GC testing, COD samples were collected and analysed in order to confirm the reduction of carbonaceous pollutants. TN samples were analysed in order to study the fate of nitrogen (converted to other than ammonia and nitrate) and ensure that nitrogen concentrations do not exceed the regulatory allowable

discharge limits. In addition, Phosphate samples were collected and analysed to ensure that phosphate was available for microbial use, and that phosphate concentrations do not exceed the regulatory allowable discharge limits.

DO samples were analysed daily to ensure that oxygen was always available for microbial use and was not limiting. In addition, the amount of oxygen used is an indicator of the health of a microbial colony (more oxygen is used by healthy colonies) and/or the rate of biodegradation.

Temperature and pH values were tested daily in order to document the operating ranges of the contactors.

Table 3-2 Laboratory Instruments

INSTRUMENT	USE	MANUFACTURER MODEL
Analytical Balance	Weighing of feed components	Denver Instrument Co. A-200D5
Electronic Scale	Weighing red rock & Soil Moist	Denver Instrument Co. DI-8KD
Gas Chromatograph with Flame Ionization Detector	Detection of EG concentrations	Hewlet Packard 5890 Series II
Fused silica capillary column, 15m, 0.53mm ID, 0.50um film thickness.	Chemical Compound Separation	SUPELCO Nukol™ Lot: 10912-03E
PH Meter	Measuring pH values	Fisher Scientific Accumet 25 pH/ion
Temperature Meter	Measuring temperature values	Fisher Scientific Accumet 25 pH/ion
Ammonia Meter	Measuring Ammonia concentrations	Fisher Scientific Accumet 25 pH/ion
Dissolved Oxygen Meter	Measuring Dissolved Oxygen concentrations	Yellow Springs Inc. 5100

Table 3-3 Analytical Methods

PARAMETERS	METHOD IDENTIFICATION	DETECTION LIMITS (mg/L)	MANUFACTURER
Chemical Oxygen Demand Manganese II Digestion	HACH method 10067	20	HACH Company
Total Nitrogen Hydroxide	HACH method 10071	> 1	HACH Company
Reactive Phosphorous	HACH method 8048	0.02	HACH Company
Nitrate, HR	HACH method 8039	0.8	HACH Company

All analytical results, observations, operation and maintenance, and other laboratory activities were documented in a laboratory log book. The log book remained in the laboratory at all times. The data log sheets were later transferred to an Excel spreadsheet. The GC data was documented immediately on an Excel spreadsheet.

Reactor Maintenance

During the period the contactors were operating, preventative maintenance was necessary to maintain a well functioning system. The clear tubing was replaced as needed and the spray nozzles were cleaned regularly and changed as needed. The flow rates were verified regularly, the timer was restarted as needed, and the feed solution containers were washed with soap and deionized (DI) water to remove accumulated material on the sides of the container.

Reproducibility & Repeatability

It is very important to prove that methods instituted during the setup and running phases of the research study can be reproduced.

Controlling variables such as temperature, pH, moisture content, and feed solution loading will assist in eliminating variations. Using the same test methods, sampling procedures, and data collection techniques improve the consistency of the results.

Laboratory procedures were adopted and implemented in order to minimize human and instrumental errors. These procedures included obtaining duplicate samples from each contactor for all 3 contactors and running tests on these samples to insure consistency of results. Additional error minimizing procedures included the testing and calibration of instruments using standards daily. In order to minimize cross contamination, clean pipettes, beakers, mixing magnets, and sample bottles were used for every sample collected.

CHAPTER IV

RESULTS / DISCUSSION

Overview

The data collected from this research was tabulated and graphed. All three contactors operated under desirable conditions over the duration of the experiment. Operating temperature remained within the 20 – 25 °C (room temperature) range and pH values ranged from 5.0 to 8.0. Figures 4-1, 4-2 and 4-3 illustrate temperature and pH values for the control contactor, low-level nutrient source contactor, and high level nutrient source contactor, respectively. Note that intermittent flow conditions existed for the low level nutrient source and high level nutrient source contactors. In order to examine and evaluate the recuperation process of the contactors under intermittent flow conditions, the low nutrient contactor was shutdown for a period of 194 hours and then restarted. The high nutrient level contactor was shutdown for 93 hours to study the drying effect on biofilm removal. Both contactors maintained temperature and pH values within the desirable range upon restart.

The collected data used in the following graphs was from the time Sta-Green[®] was added as a nutrient source (time = 1000 hours).

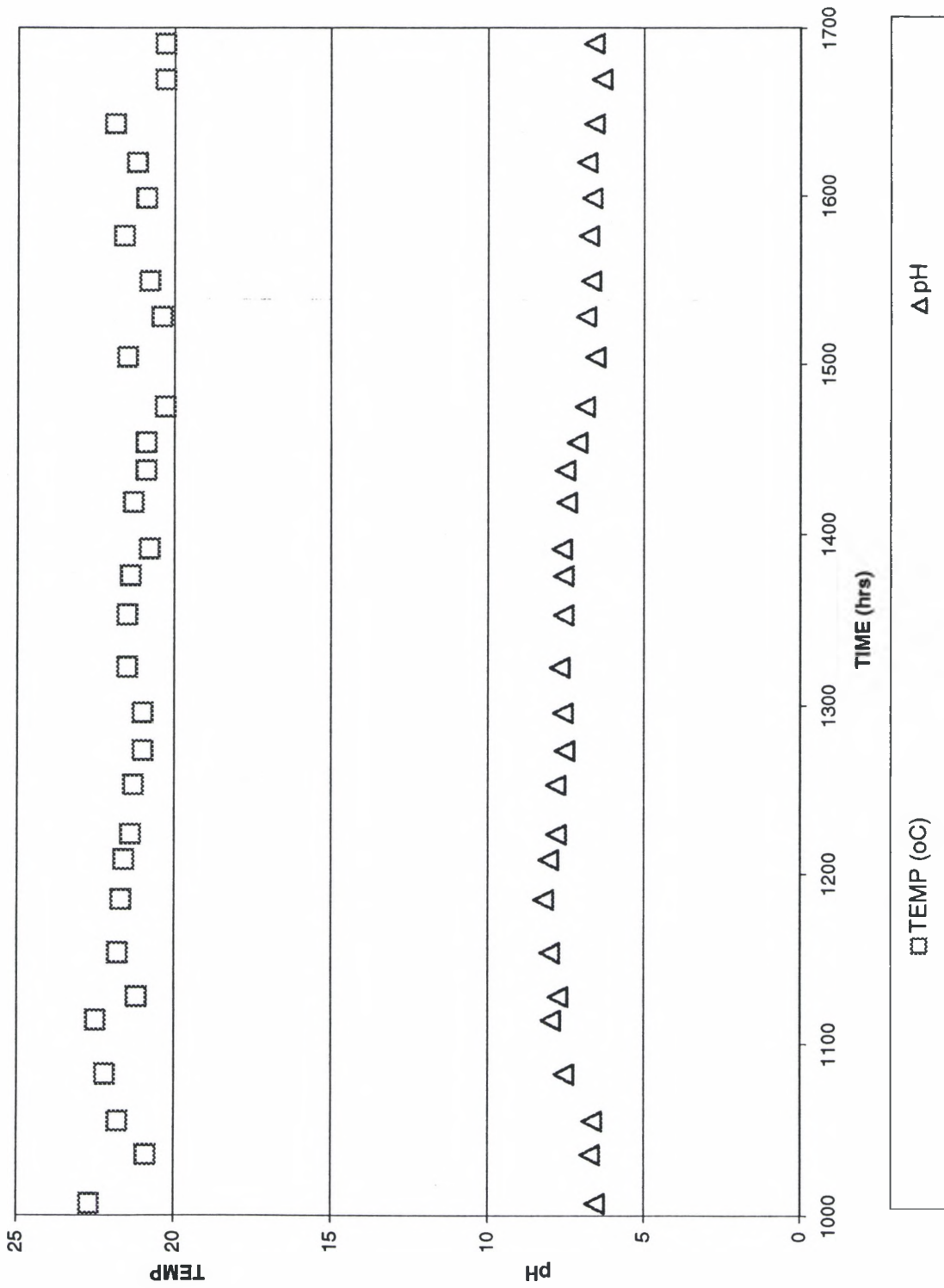


FIGURE 4-1 – CONTROL CONTACTOR, pH & TEMPERATURE

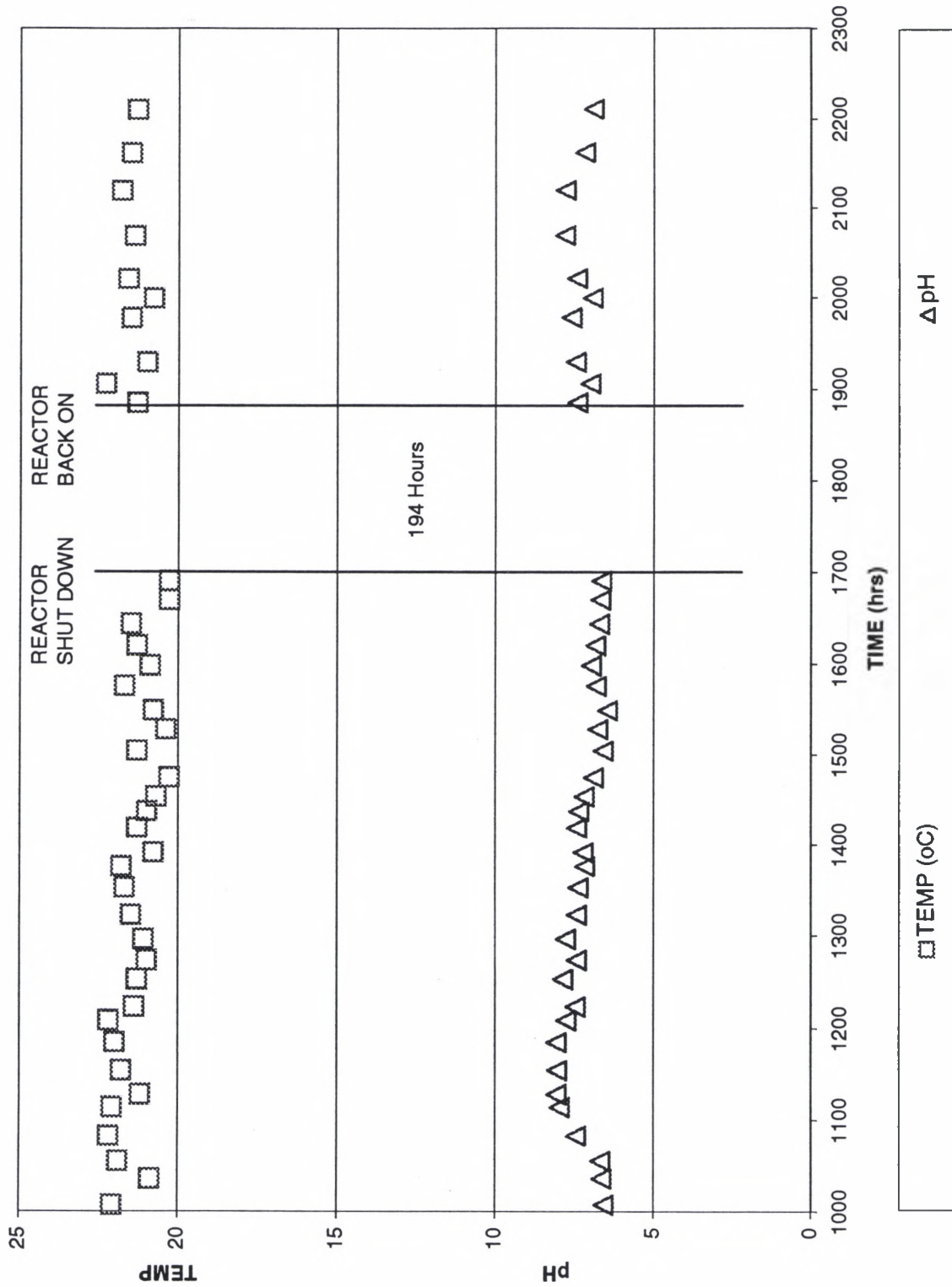


FIGURE 4-2 – LOW LEVEL NUTRIENT CONTACTOR, pH & TEMPERATURE

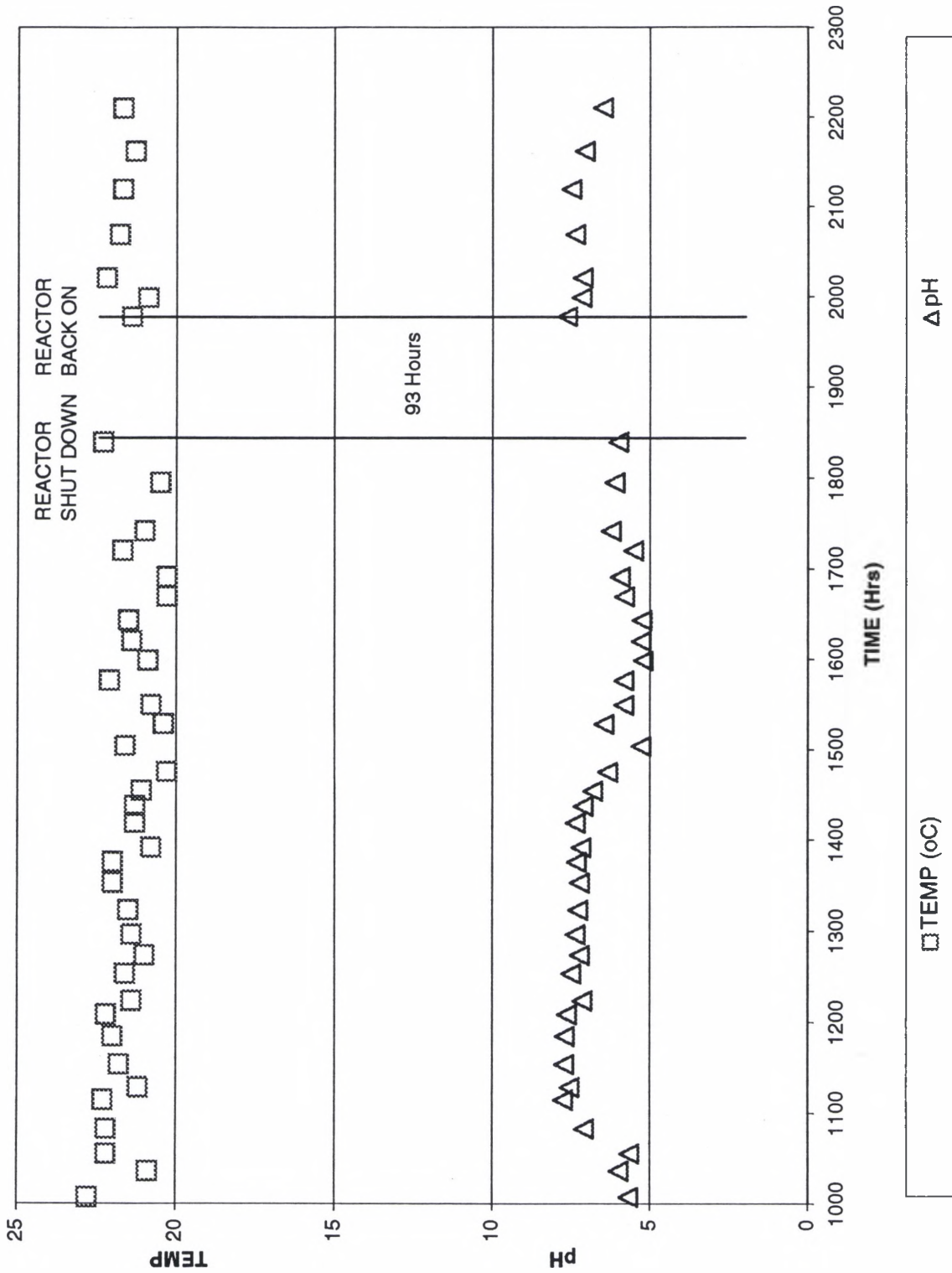


FIGURE 4-3 –HIGH LEVEL NUTRIENT CONTACTOR, pH & TEMPERATURE

Nutrient Source

In a parallel leaching study, Sta-Green[®] was found to exhibit excellent physical characteristics under hydraulic loading while providing a predictable amount of nutrients. Figure 4-4 presents the results of the leaching study. Ammonia was leached from the fertilizer at an average rate of 3.5mg/L for a period of 500 hours. An additional 300 grams of virgin fertilizer was then added to the leaching study in an effort to examine the time required for the fertilizer's effluent to stabilize. The fertilizer effluent again reached an average ammonia concentration of 3.5 mg/L within 150 hours.

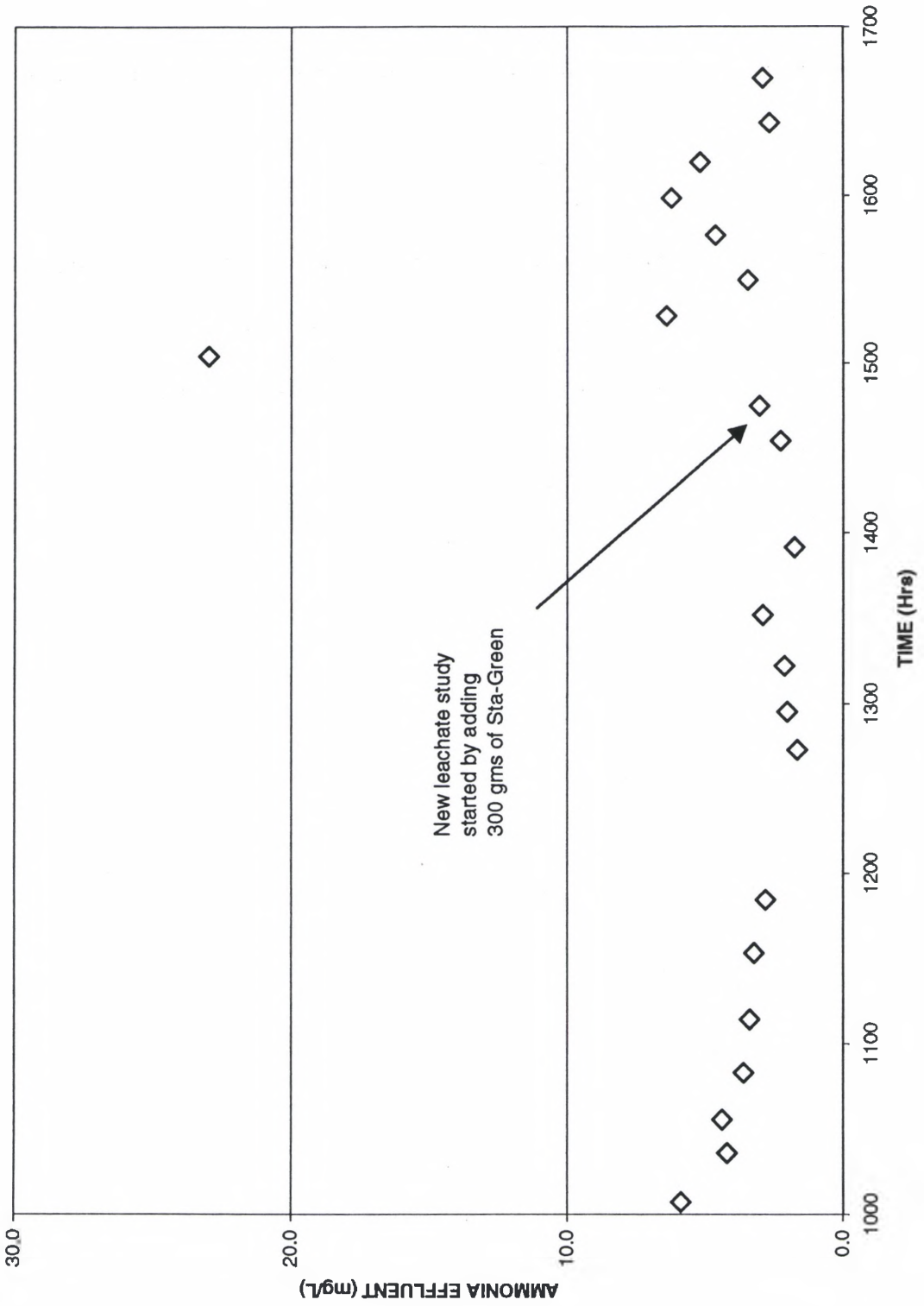


FIGURE 4-4 – LEACHATE CONTACTOR, AMMONIA EFFLUENT

Ammonia Concentrations

Leaching Study

Ammonia effluents were tested for each contactor throughout the experiment. Ammonia was a key experimental parameter in this research because it is an indication of the amount of nitrogen delivered to the microbes in the contactors. Moderate levels of leached ammonia allow the biodegradation process to occur, while excess ammonia is considered a pollutant.

Figure 4-5 shows the ammonia effluent from the control contactor to be below detection limits. These low values were expected since the only potential nutrient source was the limited amount of nitrogen in Soil-Moist.

The biodegradation of EG in the low nutrient level and the high nutrient level contactors consumed all the ammonia leached from the fertilizer except for some instances where external changes to the contactors were performed, Figure 4-6 and 4-7. Unwashed fertilizer was applied to the contactors causing ammonia effluent concentrations to reach as high as 40 mg/L. The concentrations dropped drastically to undetectable levels within 5 days from initial application. In another instance, the contactors shutdown due to an electrical malfunction. Consequently, the Sta-Green[®] located at the top of the contactors dried out. When power was restored, the contactors were turned back on and the Sta-Green[®] was rewetted, allowing effluent concentrations of ammonia to go up to as high as 12 mg/L. The concentrations dropped back to the detection limit within half a day. In addition, 100 grams of Sta-Green[®] was added to the low level nutrient contactor because

biofilm growth on the fertilizer was limiting its leaching capability. This resulted in an initial ammonia effluent concentration of 9 mg/L which dropped back to detection limits within half a day.

Low ammonia concentrations in the effluent is a good indicator that the microbial biofilm in the contactor is healthy. The absence of ammonia in the effluent would indicate the possibility of a nutrient deficient scenario where not enough nitrogen is present for microbial activity. In addition, low ammonia concentrations in the effluent is considered a good sign due to the regulated effluent limits of nitrogen into waterways.

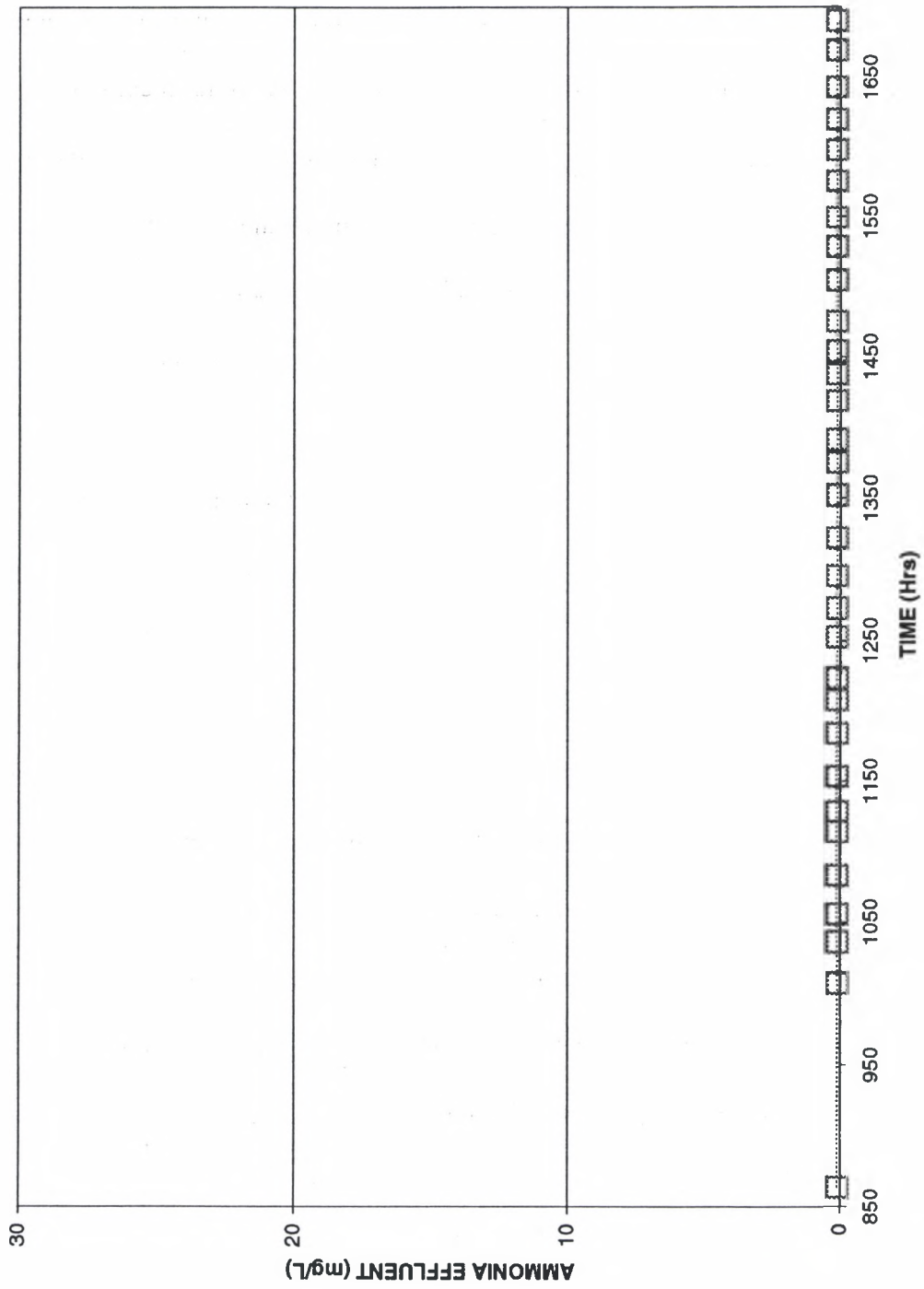


FIGURE 4-5 – CONTROL CONTACTOR, AMMONIA EFFLUENT

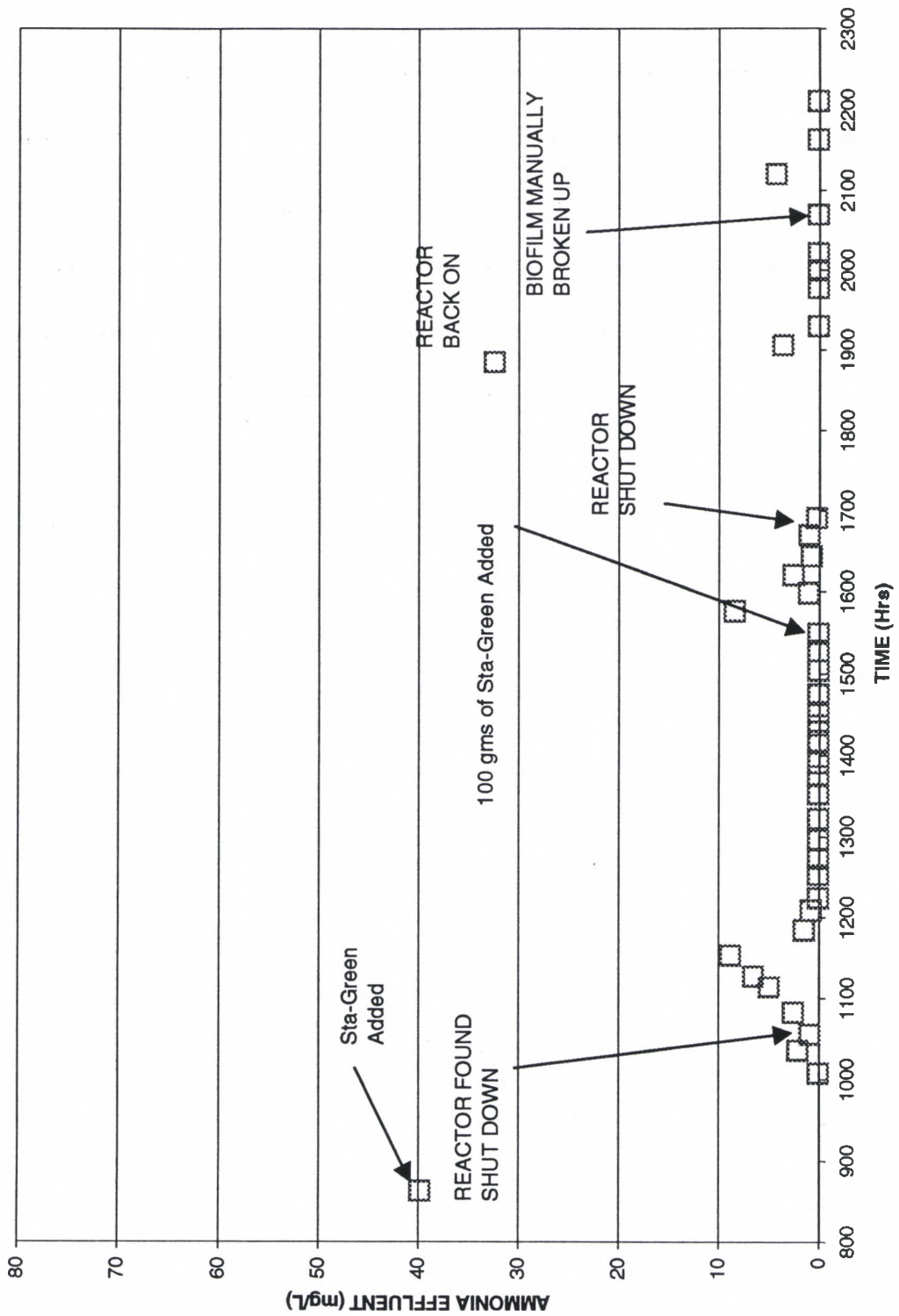


FIGURE 4-6 –LOW NUTRIENT LEVEL CONTACTOR, AMMONIA EFFLUENT

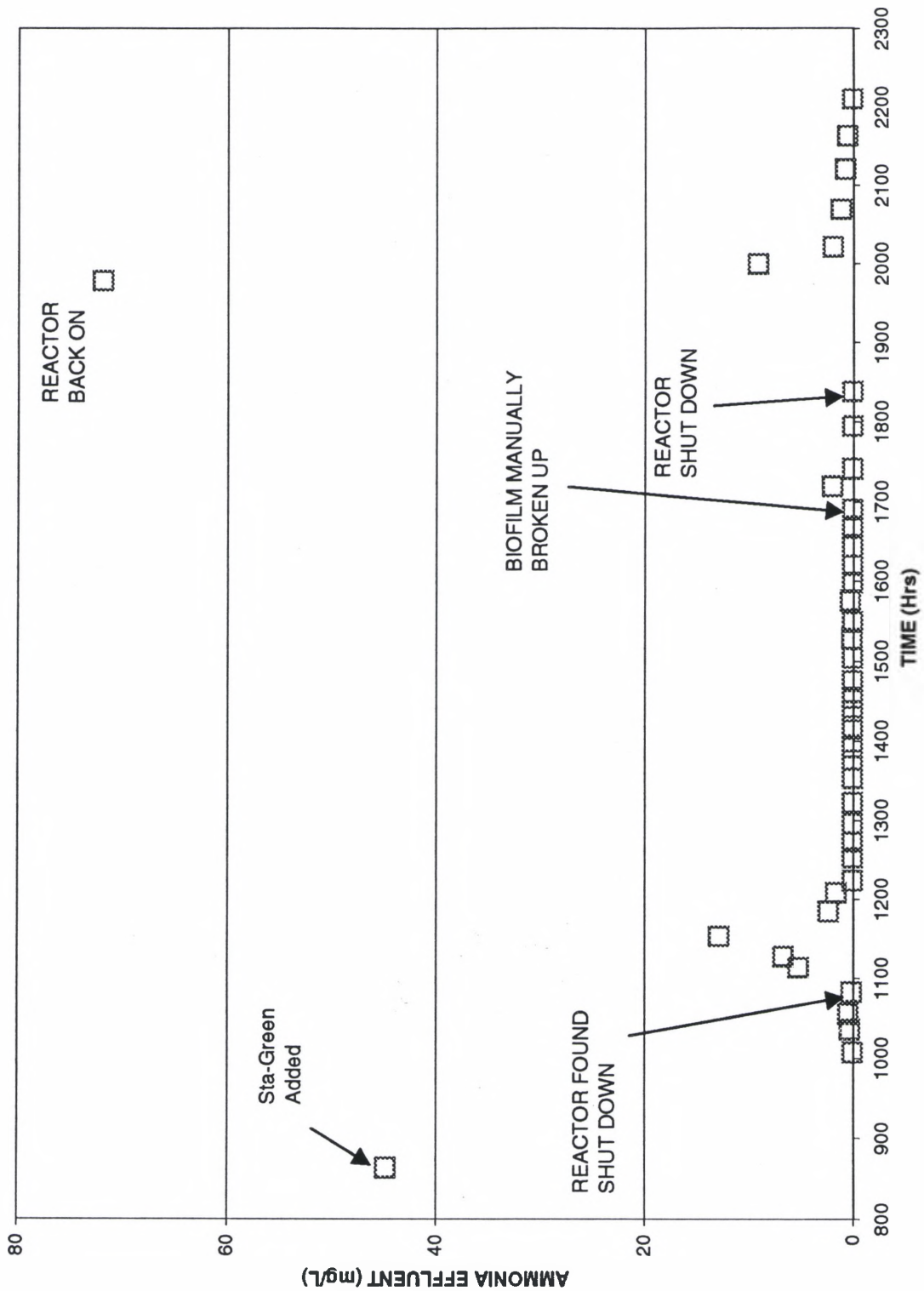


FIGURE 4-7 –HIGH NUTRIENT LEVEL CONTACTOR, AMMONIA EFFLUENT

During the last four weeks of research, the nutrient source in the low level nutrient source contactor and the high level nutrient source contactor started to exhibit a biofilm growth that affected the leaching characteristic of the fertilizer. 100 grams of Sta-Green[®] was added to the low level nutrient contactor, while the biofilm in the high level nutrient source contactor was manually broken up in an attempt to alleviate the problem. The manual breaking up of the biofilm was done by rubbing the fertilizer against each other and thus removing the biofilm coating off the surface of the fertilizer. The success of manually breaking up the biofilm was immediately exhibited by an increase in effluent ammonia levels which indicated improved leaching. However, a few days after manually breaking the biofilm, heavy concentration of biofilm returned. A second approach involved spraying the biofilm on top of the nutrients in the high level nutrient source contactor with 5 ml of 50% (by volume) hydrogen peroxide in an attempt to kill the bacteria encapsulating the nutrient source and preventing it from leaching. Unlike manual breaking, this approach did not render immediate results in the contactor effluent. After the first two alternatives failed to provide a long term solution, the high level nutrient source contactor was shut down for a period of 93 hours to dry the nutrient source and kill the attached biofilm. The low nutrient contactor was also shut down for a period of 194 hours. The concentration level of ammonia in both contactors was significantly higher after turning the contactor back on, however, the high concentration levels tapered to below the detection limit in both contactors within 72 hours.

Dissolved Oxygen Concentrations

Dissolved Oxygen (DO) tests were conducted on all three contactors on a daily basis throughout this research. A difference in concentration of DO in the effluents of the contactors indicates differences in the microbial activities among contactors. The lower the DO concentration in the effluent, the higher the microbial activity in the contactor (more oxygen is being used). Figure 4-8 illustrates the differences. The feed container (Bucket), which contain the air diffusers and had no bacterial activity, inherently had the highest levels of DO concentrations. The control reactor had the second highest DO levels indicating little bacterial activity due to the absence of a nutrient source. DO levels in the low level nutrient source contactor were next highest followed by the high level nutrient source contactor. The low DO levels in the high nutrient source contactor indicate the highest microbial activity among the contactors. Figure 4-8 also illustrates that adequate oxygen was available for microbial use throughout the research.

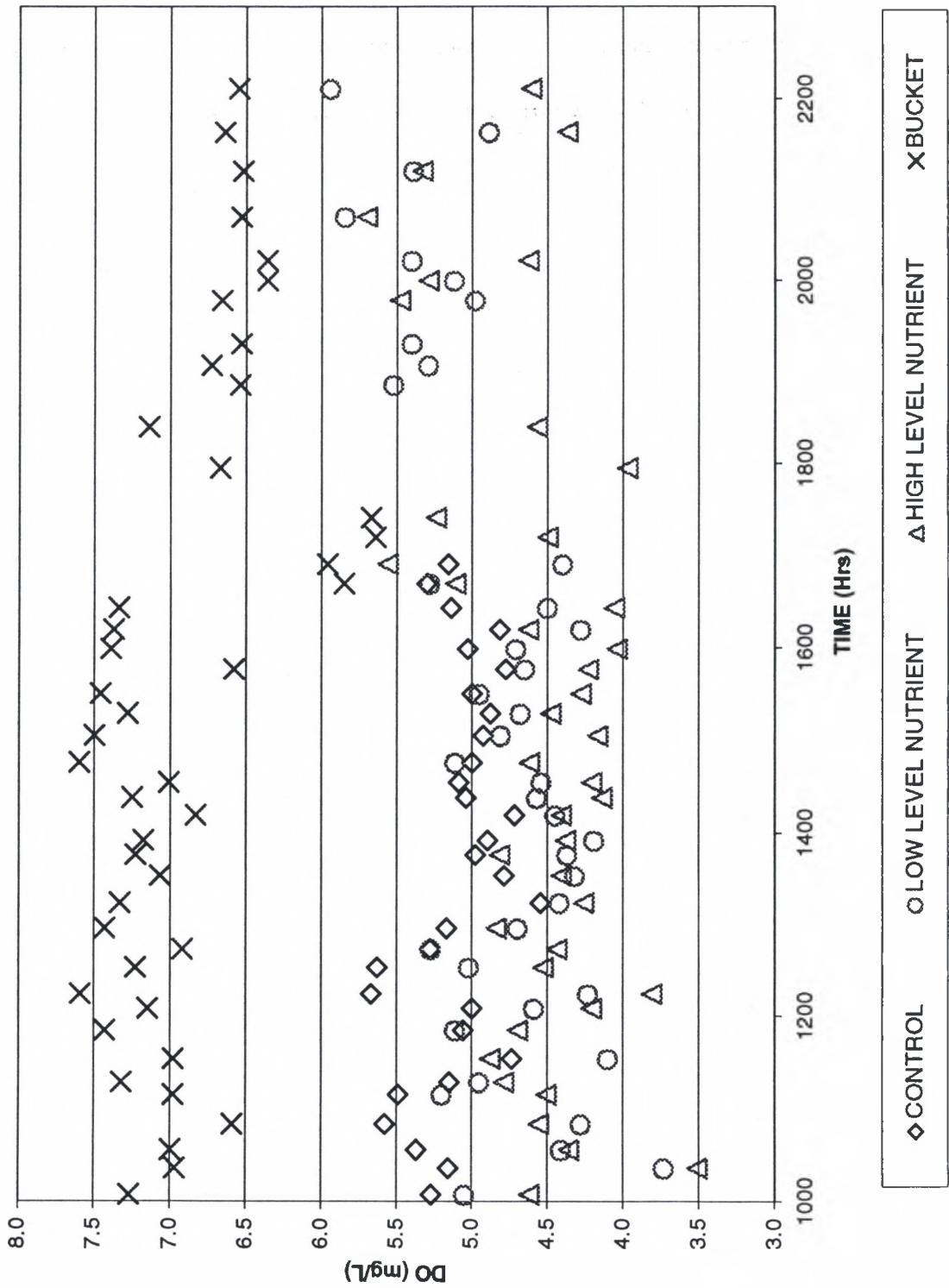


FIGURE 4-8 - DISSOLVED OXYGEN

Ethylene Glycol Concentrations

The rate of EG biodegradation is assumed to be dependent on the amount of ammonia leached from the fertilizer source. In comparing EG effluent concentrations between the low level nutrient source and the high level nutrient source contactors, Figure 4-9, the high level nutrient source contactor exhibits a high microbial activity and has the lowest EG effluent concentrations. The control contactor had the highest EG effluent levels. Figures 4-10, 4-11, and 4-12 show the percent removal of EG and ammonia for the control, low level nutrient, and high level nutrient contactors, respectively.

The control contactor exhibited a low concentration of ammonia despite the lack of a nutrient source. A laboratory test concluded that EG has no affinity to adsorb to the rock media, hence some biodegradation of EG and the low effluent of ammonia in the control contactor are attributed to the presence of low concentrations of nitrogen leaching from the Soil-Moist.

The effluent EG concentration was impacted by external changes in the contactors. The growth of a biofilm around the nutrient source, as indicated by the note "Biofilm Observed" on the graph in Figures 4-9, 4-11, and 4-12, restricted the leaching capability of the fertilizer, decreasing the amount of nutrients leached. The result was an increase in the effluent EG concentration after the biofilm encapsulating the nutrient source was manually broken, as indicated by the note "Biofilm Manually Broken" on the graph in Figures 4-9, 4-11, and 4-12.

When the nutrients became limited, an additional 100 grams of Sta-Green[®] fertilizer was added on top of the low level nutrient contactor. Replenishing the nutrients resulted in a drop in the effluent EG as indicated by the note “100 gm of Sta-Green Added” in Figures 4-9 and 4-11.

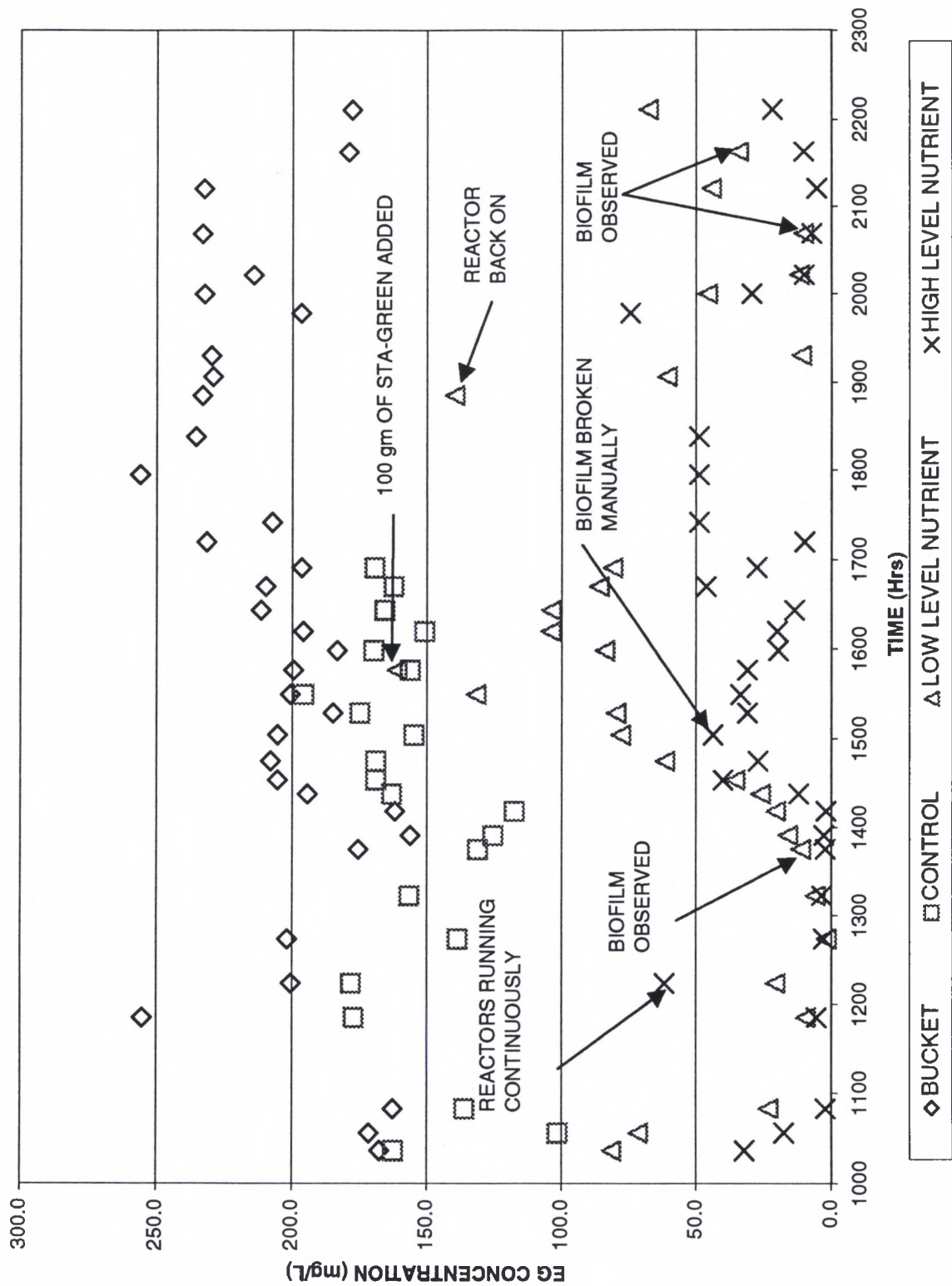


FIGURE 4-9 - EG INFLUENT & EFFLUENT CONCENTRATIONS

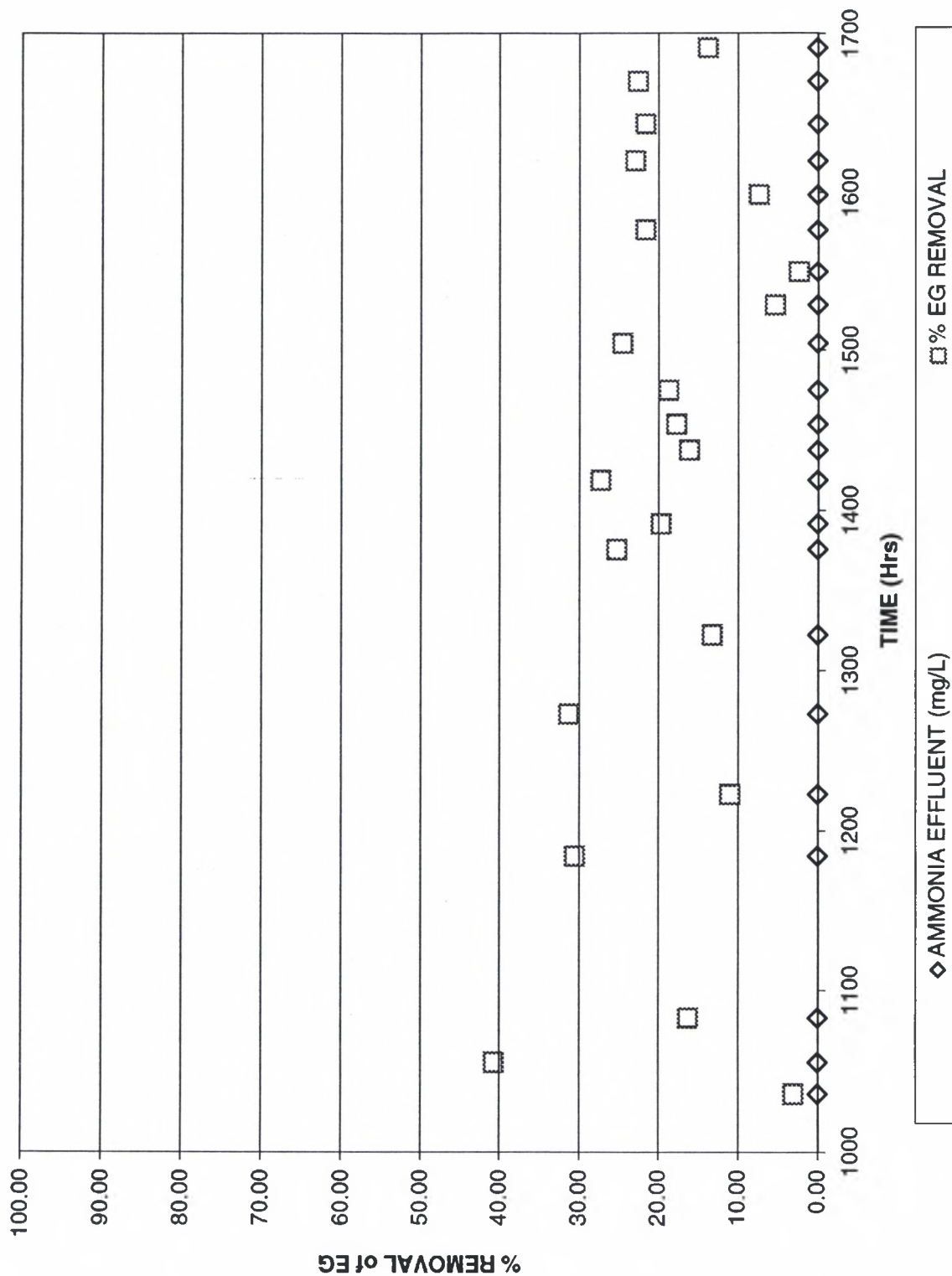


FIGURE 4-10 – % REMOVAL OF EG IN CONTROL CONTACTOR

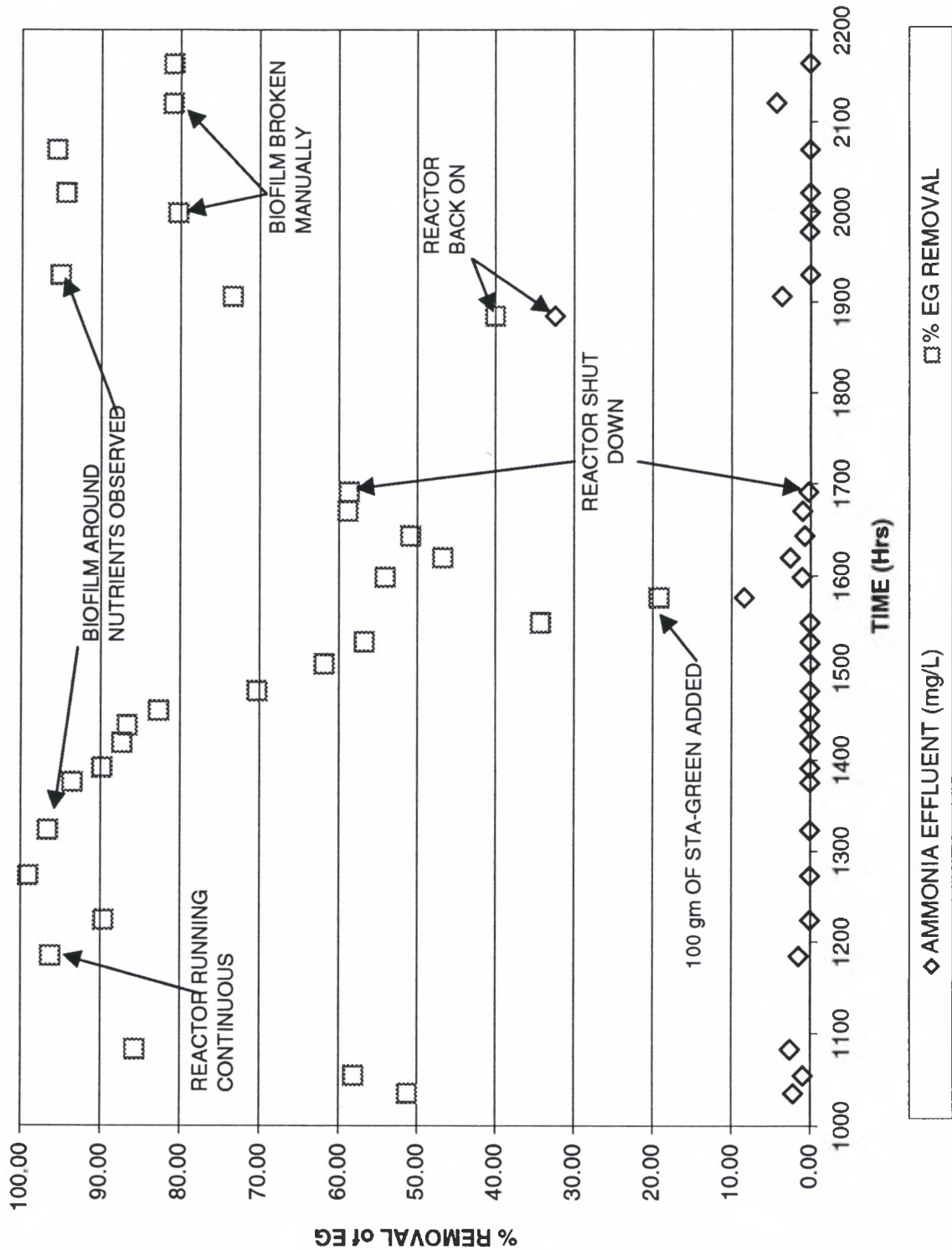


FIGURE 4-11 - % REMOVAL OF EG IN LOW LEVEL NUTRIENT CONTACTOR

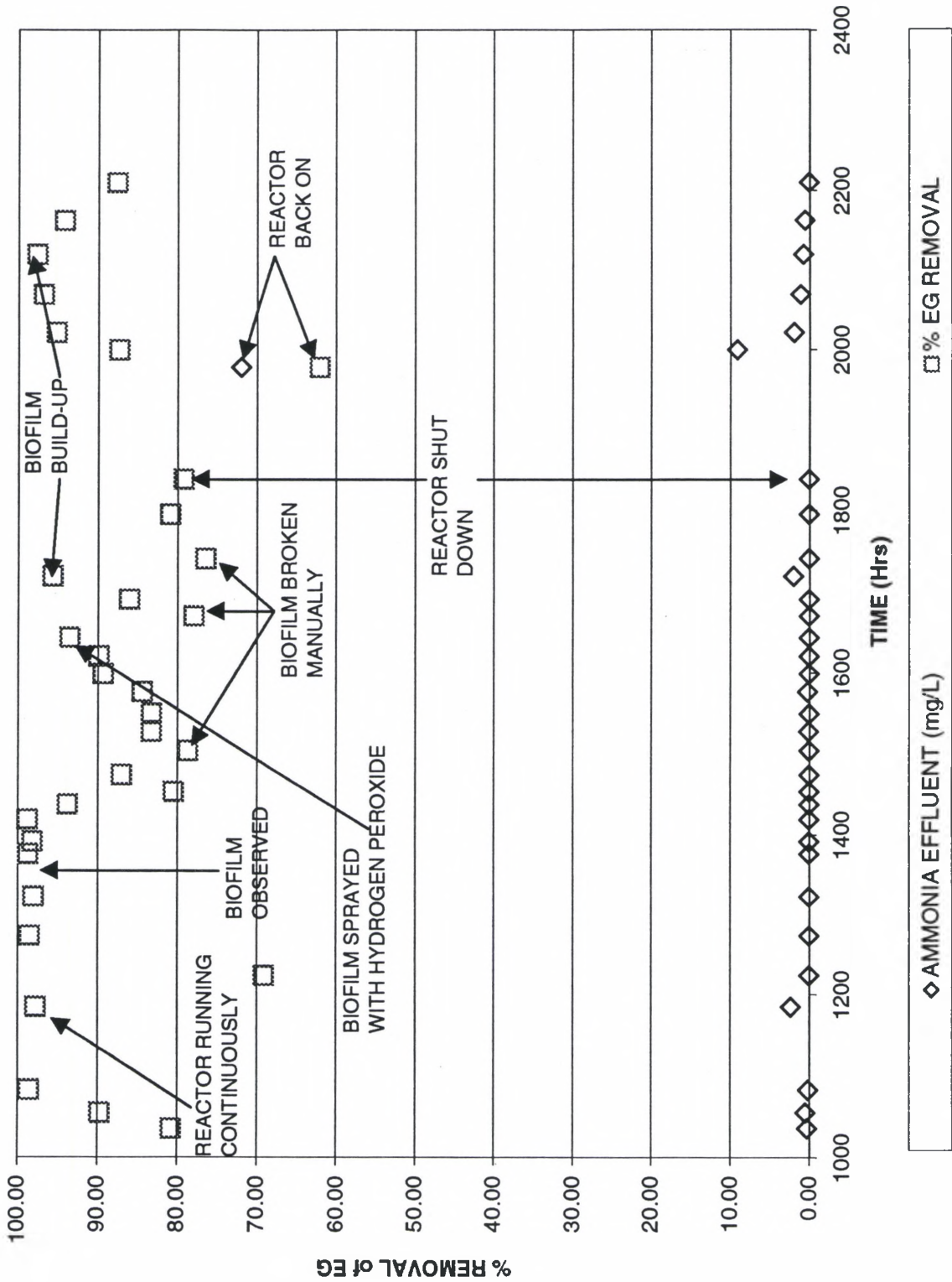


FIGURE 4-12 – % REMOVAL OF EG IN HIGH LEVEL NUTRIENT CONTACTOR

Phosphorous Concentrations

The amount of phosphorous that leached into each contactor was a function of the amount of Sta-Green[®] present in that contactor. The amount of phosphorous leached from the fertilizer is collected in the effluent from each contactor. Figure 4-13 illustrates the average concentration of phosphorous present in the effluent. The control contactor had the lowest concentrations of phosphorous followed by the low nutrient level contactor, and finally the high nutrient level.

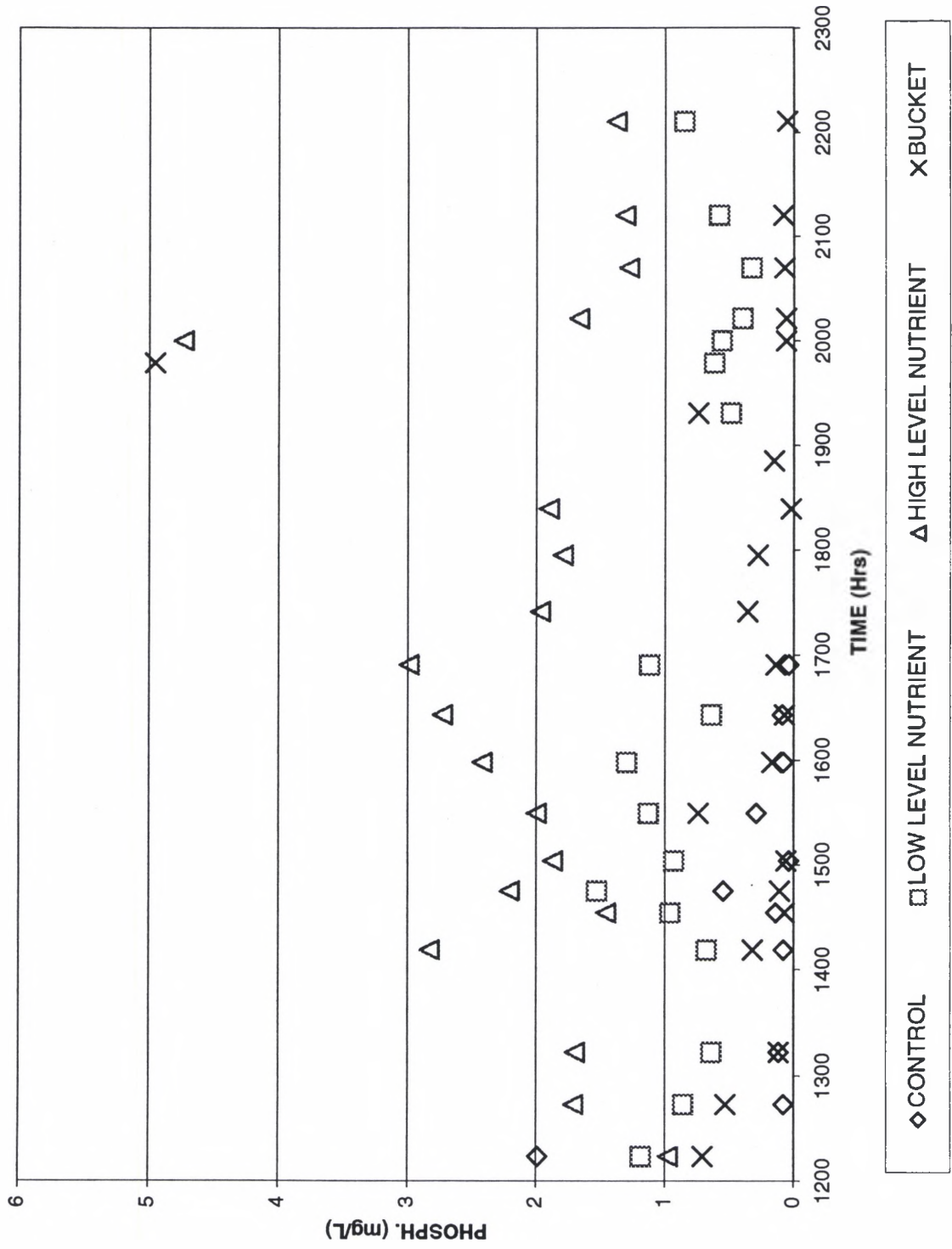


FIGURE 4-13 - PHOSPHOROUS

Additional Analysis

Additional tests were routinely conducted on the feed and contactors for the analysis of nitrate and total nitrogen. All of the measured values were below the detection limit.

Intermittent Loading

To evaluate the recuperation process of the contactors under intermittent flow conditions, the low nutrient contactor was shutdown for a period of 194 hours and then turned back on. The EG concentration level briefly rose to 140 mg/L but decreased to 11 mg/L (Pre shut-down conditions) within 96 hours (Figure 4-9). This indicates a healthy microbial population and the presence of sufficient moisture due to the Soil-Moist additive to keep the population active during non-flow conditions.

Passive vs. Soluble Nutrient Addition

A comparison between the data obtained from the high level nutrient source contactor and the data from a contactor system with nutrients dissolved in the feed (idealized) was conducted. In the idealized contactor, the effluent concentrations of EG were between 25 mg/L and the detection limit of 5 mg/L. In most cases the high level nutrient source contactor had similar results to the idealized contactor and in some cases exceeded the idealized contactor in EG removal efficiency.

Theoretical Nutrient Requirements

A mathematical calculation was performed to compare the bacteria's use of nutrients and the theoretical molar ratio of C:N:P (100:5:1) (M. Hammer & M. Hammer, 1996). The

purpose of this comparison is to examine if the amount of nutrients supplied to the contactors was adequate or limiting. A sample calculation is shown and the results are tabulated in Appendix A, Table A-8.

Sample Calculation:

1. The Molecular Weight of EG ($C_2H_6O_2$) is 62 grams and the Molecular Weight of Ammonia (NH_3) is 17 grams; and for sample time = 1619.6 hours, the following low level nutrient source contactor data was obtained:

Influent Ammonia from parallel leachate study = A = 5.2 mg/L (Table A-5)

Effluent Ammonia for low level nutrient source = A_1 = 2.6 mg/L (Table A-2)

EG Influent level = B = 196 mg/L (Table A-6)

EG Effluent for low level nutrient source = B_1 = 104 mg/L (Table A-6)

2. The difference between influent and effluent concentrations was calculated:

$$A_{LOW} = A - A_1 = 5.2 - 2.6 = 2.6 \text{ mg/L} = 0.0026 \text{ gms/L (Ammonia)}$$

$$B_{LOW} = B - B_1 = 196 - 104 = 92 \text{ mg/L} = 0.092 \text{ gms/L (EG)}$$

3. The molar Carbon and Nitrogen concentration was calculated:

$$\begin{aligned} \text{Carbon}_{LOW} &= 0.092 \text{ gms } C_2H_6O_2 / L \times 24 \text{ gms C} / 62 \text{ gms } C_2H_6O_2 \\ &\quad \times 1 \text{ mole C} / 12 \text{ gms C} = 0.003 \text{ moles C} / \text{Liter.} \end{aligned}$$

$$\begin{aligned} \text{Nitrogen}_{LOW} &= 0.0026 \text{ gms } NH_3 / L \times 14 \text{ gms N} / 17 \text{ gms } NH_3 \\ &\quad \times 1 \text{ mole N} / 14 \text{ gms N} = 0.00015 \text{ moles N} / \text{Liter.} \end{aligned}$$

4. The ratio of Carbon to Nitrogen was found:

$$\begin{aligned} \text{Carbon}_{\text{LOW}} / \text{Nitrogen}_{\text{LOW}} &= 0.003 \text{ moles C / Liter} / 0.00015 \text{ moles N / Liter} \\ &= 20 \text{ moles C / moles N} \end{aligned}$$

An average experimental ratio of 28:1 and 32:1 was obtained for the low level nutrient source and the high level nutrient source respectively. The high level nutrient contactor exhibits a higher C:N ratio than low level nutrient contactor due to the surface area covered by the fertilizer in each of the contactors. The 100 grams of Sta-Green® fertilizer used in the low level contactor was spread across the top of the unit but did not cover the entire surface area. The 150 grams of Sta-Green® fertilizer used in the high level contactor was enough to cover the entire surface area on top of the rock bed. While the leaching rate of both contactors is the same, more ammonia was leached into the high level contactor due to a larger surface area covered by the fertilizer. The experimental values of C:N ratios obtained from the research are larger than their theoretical counterparts, indicating the possibility of the presence of a secondary nitrogen source in both contactors.

CHAPTER V

SUMMARY AND CONCLUSION

Summary

The objective of this research was to analyze the potential of the passive addition of a solid form, slow-release, nutrient source to allow for the aerobic microbiological degradation of predominantly carbon-polluted storm water in a subsurface microbiological contactor. The general experimental plan involved the construction and operation of three (3) physically identical microbiological contactors that ran in parallel. One of the contactors served as a control and had no nutrient source added while the other two had a solid form, slow-release nutrient source added. The low nutrient level contactor initially had 100 grams of Sta-Green[®] fertilizer and the high nutrient level contactor had 150 grams of the same fertilizer. The experiment was conducted in two phases. Phase I involved operating the contactors until equilibrium was achieved (percent removal of EG was constant over 5 days). A mathematical calculation was performed to compare the bacterial use of nutrients and the theoretical molar ratio of C:N:P (100:5:1). The purpose of this comparison is to examine if the amount of nutrients supplied to the contactors was adequate or limiting. A comparison between the high level nutrient source contactor and a contactor system with nutrients dissolved in the feed (idealized) was also conducted.

Phase II involves shutting down the low level nutrient contactor for a period of 194 hours. The purpose of this phase was to evaluate the recuperation process of the contactor under intermittent flow conditions.

All three contactors operated under desirable conditions over the duration of the experiment. Operating temperature remained within the 20 – 25 °C (room temperature) range and pH values ranged from 5.0 to 8.0.

The control contactor achieved approximately 15% to 30% EG removal. The low level nutrient source contactor was inconsistent, for various reasons discussed below, but could achieve EG removals in the 50% or better range, while the high level nutrient source contactor typically achieved 75% to 100% EG removal efficiencies.

From Phase I, it was determined that the biodegradation of EG in the low nutrient level and the high nutrient level contactors consumed almost all of the ammonia leached from the fertilizer except for some instances where external changes to the contactors occurred. However, the levels of ammonia concentrations in the effluent followed a predictable pattern. Ammonia levels increased when the contactors were restarted or when additional fertilizer was added, and decreased when the biofilm restricted the leaching characteristics of the fertilizer source. In addition, the low concentrations of ammonia in the effluent, resulting from microbial activity, alleviates the problem of excess effluent ammonia which is considered a pollutant.

The DO concentration in the contactors effluent indicated that oxygen was not a limiting factor in this research. Furthermore, the level of DO corresponded to the quantity of nutrient within the contactors and the EG removal efficiency.

EG effluent concentrations indicated that the high level nutrient source contactor exhibited the best EG removal, followed by the low level nutrient source and the control contactor. In addition, the high level nutrient source contactor rendered similar or better results than the contactor system with nutrients dissolved in the feed (idealized). The comparison of the data for the two contactors indicated that both contactor effluent concentrations of EG were between 25 mg/L and the detection limit of 5 mg/L.

The amount of phosphorous that leached into each contactor was a function of the amount of Sta-Green[®] present in that contactor. The control contactor had the lowest concentrations of phosphorous followed by the low nutrient level contactor, and finally, the high nutrient level. Effluent concentrations indicated that phosphorous was not limiting in this study.

All of the data collected for nitrate and total nitrogen tests were below detection limit. The very low levels of nitrate indicated that aerobic nitrification and anaerobic denitrification processes were occurring.

In phase II, the recuperation process of the contactors under intermittent flow conditions was examined and showed that the contactor recuperated back to pre-shut-down

conditions within 48 hours of being turned back on. This was exhibited by low ammonia effluent concentrations and high EG percent removals. A healthy microbial colony and the presence of sufficient moisture due to the Soil-Moist additive could be accredited for the recuperation of the contactor. Also in Phase II, the high nutrient level contactor was shutdown for 93 hours to study the drying effect on biofilm removal.

The average experimental carbon to nitrogen ratio was found to be in the vicinity of 30:1 as compared to the theoretical ratio of 20:1. The higher than theoretical values obtained indicate the possibility of the presence of a secondary source of nitrogen. The source of nitrogen could be from the Soil-Moist, which leaches low amounts of nitrogen, or from the recycling of nutrients in the contactors. The recycling of nutrients is observed when live bacteria make use of dead bacteria as a nutrient source. Another possibility of the high C:N ratio obtained could be accredited to a special form of bacteria that survives on limited nitrogen supplies.

Conclusions

This research proves that the passive addition of a solid form, slow-release, nutrient source technology improves the aerobic microbiological degradation of EG and possibly other predominantly carbon-polluted storm water in a subsurface microbiological contactor. Larger scale studies using stormwater in field conditions is warranted.

The experimental contactor system produced similar results to an idealized contactor and was proven to recuperate well under intermittent flow conditions. The components of the

contactor system are commercially available at a relatively economical price. In addition, the high nutrient level contactor provided 88% removal efficiency, on average, while producing little or no ammonia in the effluent.

Additional studies on the nutrient source as well as effects of temperature variations on the contactor should be conducted. The growth of a biofilm around the nutrient source was observed in the laboratory study. This growth will limit the leaching capability of the fertilizer and will impact the concentrations of EG in the effluent. The nutrients could become a limiting factor in the contactor due to the bacterial biofilm growth around the fertilizer. Additional studies are required to provide engineering guidance to alleviate this problem.

In addition, the temperature flux in nature will affect the biodegradation rates of the microorganisms. For every 10 °C decrease in temperature, the microbial activity is typically cut in half. This will result in an increase in the concentration of EG in the effluent. If economically and logistically feasible, this problem could be resolved by physically doubling the size of the contactor for every 10 °C decrease in temperature. Additional research needs to be conducted in order to study the effluent concentrations of EG under low temperature conditions.

Further research into the polymer coated fertilizer and the relative nitrogen and phosphorous concentrations is required. The physical and leaching properties of the fertilizer under cold temperatures is another concern that needs to be addressed through

additional studies. Moreover, a fertilizer with a lower phosphorous content might be considered as an alternative for reducing phosphorous concentrations in the effluent.

Due to the high BOD demand exerted by EG degradation, dissolved oxygen might become a problem in the reactor in nature. The absence of a continuous air supply could render the electron acceptor (oxygen in this case) limiting and additional studies to assess this possibility are recommended. A waterfall-type structure could be built in front of the contactor to provide mixing of the influent and the needed dissolved oxygen to degrade EG.

Finally, the proposed subsurface microbiological contactor is an engineered system that requires modifications to design parameters for field applications. The laboratory experiment provides organic loading data that could be used to estimate the size of the proposed pilot scale contactor. Additional organic loading ($\text{lb BOD}/\text{ft}^3$) factors needing consideration include the pollutant of concern, temperature, average and extreme BOD concentrations, and permit effluent requirements.

Hydraulic loading ($\text{gal}/\text{min. ft}^2$) should also be considered for the pilot scale contactor.

Minimum hydraulic loading should not be a factor of concern due to the presence of Soil-Moist that provides the minimum required moisture for microbial survival. However, maximum hydraulic loading should be taken into consideration in order to insure that the biomass is not sloughed due to excessive flow.

In addition to the above mentioned design parameters, the amount of nutrients supplied to the contactor should also be taken into consideration depending on the proposed site. Site locations and temperature variation may very well effect the kind of nutrient used and the proposed amounts. Nutrients could be supplied into the influent stream by sprinkling the fertilizer on top of the contactor, as in this experiment, or by a more sophisticated method of delivery such as a nutrient well.

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VITA

Roger Antoine Azar was born on November 3rd 1970 in the West African nation, Liberia. Mr. Azar relocated to Beirut, Lebanon where he attended high school. After graduating from high school, Mr. Azar briefly took college courses in Civil Engineering in an American University in Beirut. After a grueling civil war tore up Lebanon, Mr. Azar immigrated to the United States of America in 1991. In the U.S, Mr. Azar attended the University of Dayton and completed a degree in Civil Engineering in 1995.

After graduation, Mr. Azar got a full-time job as a Civil and Environmental engineer in a Dayton company and worked as a design and compliance engineer. Mr. Azar is credited with the clean-up design of a radioactive-contaminated segment of the Miami-Erie Canal in Miamisburg, Ohio. He also designed numerous landfill caps, liners, detention/retention ponds, and hazardous water excavation projects. Mr. Azar managed two endangered species projects at Wright-Patterson AFB.

Mr. Azar is an Engineer in Training (E.I.T) and is planning to take the Professional Engineering (P.E) exam in April 1999.

In December 1995, Mr. Azar was granted U.S citizenship. Mr. Azar is fluent in English, Arabic, and French and enjoys outdoors activities particularly hunting, fishing, hiking, and off-road biking.

APPENDIX A

TABLES

TABLE A-1

TIME (Hrs)	CONTROL CONTACTOR							
	COD (mg/L)	DO (mg/L)	TEMP (°C)	PH	NH ₃ (mg/L)	NITRATE (mg/L)	PHOSPH (mg/L)	TN (mg/L)
863.3					0.1			
1007.3		5.3	22.7	6.58	0.1			
1035.8	149	5.2	20.9	6.73	0.1	0.3	2	0
1055.3	138	5.4	21.8	6.67	0.1	0.4		
1082.8	141	5.6	22.2	7.56	0.1	0.4		1
1114	52	5.5	22.5	7.98	0.1	0.5		
1127.8	15	5.2	21.2	7.76	0.1	0.7	0	2
1153.3	0	4.7	21.8	8.03	0.1	0.6		
1184.3	79	5.1	21.7	8.22	0.1	0.6		2
1208		5.0	21.6	8.05	0.1			
1223.3	147	5.7	21.4	7.81	0.1	0.7	2	2
1252.55		5.6	21.3	7.83	0.1			
1273	135	5.3	21	7.55	0.1	1.2	0	1
1295.5		5.2	21	7.6	0.1			
1322.3	64	4.6	21.5	7.7	0.1	0.9	0	2
1352.3		4.8	21.5	7.59	0.1			
1375.3	114	5.0	21.4	7.59	0.1	0.9		1
1391.3	140	4.9	20.8	7.63	0.1			
1418.5	102	4.7	21.3	7.48	0.1	0.8	0	1
1437.5	149	5.0	20.9	7.53	0.1	0.8		0
1453.8	142	5.1	20.9	7.15	0.1	0.4	0	1
1474.8	171	5.0	20.3	6.9	0.1	0.5	1	1
1504	139	4.9	21.5	6.57	0.1	0.5	0	0
1528	167	4.9	20.4	6.87	0.1	0.5		0
1549.2	147	5.0	20.8	6.71	0.1	0.4	0	2
1576		4.8	21.6	6.77	0.1			
1598.3	177	5.0	20.9	6.67	0.1	0.3	0	0
1619.6		4.8	21.2	6.83	0.1			
1643.1	294	5.1	21.9	6.6	0.1	0.4	0	1
1669.7		5.3	20.3	6.35	0.1			
1690.7		5.2	20.3	6.6	0.1	0.3	0	0

TABLE A-2

TIME	LOW LEVEL NUTRIENT CONTACTOR							
	COD (mg/L)	DO (mg/L)	TEMP (°C)	PH	NH ₃ (mg/L)	NITRATE (mg/L)	PHOSPH (mg/L)	TN (mg/L)
863.3					39.9			
1007.3		5.1	22.1	6.58	0.1			
1035.8	75	3.7	20.9	6.66	2.15	0.5	3	1
1055.3	83	4.4	21.9	6.69	0.957	0.9		
1082.8	0	4.3	22.2	7.45	2.6	0.3		6
1114	0	5.2	22.1	7.97	5	0.3		
1127.8	9	5.0	21.2	8.07	6.56	0.5	3	10
1153.3	0	4.1	21.8	8.06	8.89	1		
1184.3	101	5.1	22	8.07	1.49	0.1		3
1208		4.6	22.2	7.77	0.85			
1223.3	39	4.2	21.4	7.48	0.1	0.4	1	1
1252.55		5.0	21.3	7.86	0.1			
1273	23	5.3	21	7.44	0.1	0.6	1	1
1295.5		4.7	21.1	7.78	0.1			
1322.3	17	4.4	21.5	7.44	0.1	0.2	1	2
1352.3		4.3	21.7	7.38	0.1			
1375.3	0	4.4	21.8	7.19	0.1	0		2
1391.3	45	4.2	20.8	7.24	0.1			
1418.5	57	4.5	21.3	7.43	0.1	0.3	1	1
1437.5	6	4.6	21	7.37	0.1	0.4		0
1453.8	22	4.5	20.7	7.2	0.1	0.3	1	2
1474.8	70	5.1	20.3	6.91	0.1	0.4	2	2
1504	52	4.8	21.3	6.6	0.1	0.2	1	0
1528	78	4.7	20.4	6.77	0.1	0.2		1
1549.2	136	5.0	20.8	6.46	0.1	0.3	1	1
1576		4.7	21.7	6.83	8.47			
1598.3	88	4.7	20.9	6.97	1.09	0.8	1	2
1619.6		4.3	21.3	6.84	2.61			
1643.1	109	4.5	21.5	6.72	0.76	0.5	1	1
1669.7		5.3	20.3	6.68	0.989			
1690.7		4.4	20.3	6.65	0.306	0.4	1	0
1719.7								
1741.1								
1794.7								
1838.7								
1884.7	183	5.5	21.3	7.42	32.5			
1905.7		5.3	22.3	7.01	3.65			
1929.7		5.4	21	7.47	0.1		0	
1977.7	27	5.0	21.5	7.61	0.133		1	
1999.2		5.1	20.8	6.94	0.1		1	
2021		5.4	21.6	7.44	0.1		0	
2069		5.8	21.4	7.81	0.1		0	
2120		5.4	21.8	7.79	4.33		1	
2162.5		4.9	21.5	7.19	0.1			
2210.5		5.9	21.3	6.9	0.1		1	

TABLE A-3

TIME	HIGH LEVEL NUTRIENT CONTACTOR							
	COD (mg/L)	DO (mg/L)	TEMP (°C)	PH	NH ₃ (mg/L)	NITRATE (mg/L)	PHOSPH (mg/L)	TN (mg/L)
863.3					44.9			
1007.3		4.6	22.8	5.7	0.1			
1035.8	30	3.5	20.9	6	0.35	0.4	1	0
1055.3	48	4.4	22.2	5.67	0.516	0.4		
1082.8	0	4.6	22.2	7.1	0.188	0		2
1114	0	4.5	22.3	7.77	5.27	0.3		
1127.8	0	4.8	21.2	7.56	6.74	1.5	4	15
1153.3	0	4.9	21.8	7.73	12.9	0.9		
1184.3	0	4.7	22	7.71	2.38	0.1		6
1208		4.2	22.2	7.65	1.67			
1223.3	71	3.8	21.4	7.15	0.1	0.4	1	1
1252.55		4.5	21.6	7.51	0.1			
1273	48	4.4	21	7.25	0.1	0.9	2	1
1295.5		4.8	21.4	7.38	0.1			
1322.3	19	4.3	21.5	7.29	0.1	0.3	2	1
1352.3		4.4	22	7.24	0.1			
1375.3	0	4.8	22	7.35	0.1	0.1		2
1391.3	23	4.4	20.8	7.19	0.1			
1418.5	30	4.4	21.3	7.38	0.1	0.1	3	2
1437.5	17	4.1	21.3	7.13	0.1	0.6		1
1453.8	0	4.2	21.1	6.82	0.1	0.5	1	1
1474.8	61	4.6	20.3	6.34	0.1	0.4	2	2
1504	75	4.2	21.6	5.3	0.1	0.4	2	1
1528	69	4.5	20.4	6.47	0.14	0.3		1
1549.2	70	4.3	20.8	5.83	0.1	0.2	2	1
1576		4.2	22.1	5.83	0.3			
1598.3	54	4.0	20.9	5.22	0.1	0.4	2	1
1619.6		4.6	21.4	5.29	0.1			
1643.1	113	4.1	21.5	5.25	0.1	0.6	3	1
1669.7		5.1	20.3	5.82	0.1			
1690.7		5.6	20.3	5.96	0.1	0.6	3	1
1719.7		4.5	21.7	5.53	2.05			
1741.1		5.2	21	6.24	0.1	0.3	2	1
1794.7		4.0	20.5	6.13	0.1	0.45	2	1
1838.7	74	4.6	22.3	6	0.1		2	
1884.7								
1905.7								
1929.7								
1977.7		5.5	21.4	7.64	72			
1999.2		5.3	20.9	7.18	9.17		5	
2021		4.6	22.2	7.14	1.98		2	
2069		5.7	21.8	7.38	1.18		1	
2120		5.3	21.7	7.5	0.8		1	
2162.5		4.4	21.3	7.07	0.6			
2210.5		4.6	21.7	6.5	0.1		1	

TABLE A-4

TIME	BUCKET						
	COD (mg/L)	DO (mg/L)	TEMP (°C)	PH	NITRATE (mg/L)	PHOSPH (mg/L)	TN (mg/L)
863.3							
1007.3		7.3	21.8	6.3			
1035.8	172	7.0	21.5	7.2	0.4	3	0
1055.3	193	7.0	21.5	7.22	0		
1082.8	150	6.6	22	7.07	0.9		2
1114	29	7.0	21.9	7.67	0.6		
1127.8	42	7.3	20.9	7.14	1.6	0	2
1153.3	17	7.0	21.3	7.8	0		
1184.3	136	7.4	20.8	8.46	0.9		3
1208		7.2	21.5	7.76			
1223.3	201	7.6	21	7.37	1	1	2
1252.55		7.2	21.2	8.03			
1273	252	6.9	21.1	7.18	1.1	1	1
1295.5		7.4	20.7	7.78			
1322.3	210	7.3	20.8	7.11	0.7	0	2
1352.3		7.1	21.2	7.76			
1375.3	128	7.2	21.3	7.04	0.7		2
1391.3	244	7.2	21	7.82			
1418.5	215	6.8	20.8	7.14	0.5	0	2
1437.5	175	7.3	20.4	7.76	0.8		0
1453.8	106	7.0	20.5	6.72	0.6	0	0
1474.8	186	7.6	20	7.14	0.3	0	1
1504	223	7.5	20.5	6.85	0.4	0	0
1528	200	7.3	21.9	6.95	0.3		0
1549.2	212	7.5	20.8	6.93	0.4	1	1
1576		6.6	21.5	6.84			
1598.3	222	7.4	21.5	6.94	0.3	0	1
1619.6		7.4	20.7	6.84			
1643.1	204	7.3	20.8	6.72	0.3	0	1
1669.7		5.9	20.1	6.84			
1690.7		6.0	20.4	6.85	0.3	0	0
1719.7		5.6	21.1	6.58			
1741.1		5.7	20.1	6.9	0.3	0	1
1794.7		6.7	20	6.95	0.3	0	0
1838.7	138	7.1	20.4	6.75		0	
1884.7	234	6.5	20.8	6.87		0	
1905.7		6.7	21	6.91			
1929.7		6.5	20.6	7.23		1	
1977.7	222	6.7	20.9	7.27		5	
1999.2		6.4	20.5	7.05		0	
2021		6.4	20.8	7.66		0	
2069		6.5	21.2	7.59		0	
2120		6.5	20.3	7.65		0	
2162.5		6.6	20.5	7.77			
2210.5		6.6	20.3	7		0	

TABLE A-5

TIME	LEACHATE
(Hrs)	NH₃ (mg/L)
863.3	
1007.3	5.9
1035.8	4.2
1055.3	4.4
1082.8	3.6
1114	3.4
1127.8	
1153.3	3.2
1184.3	2.8
1208	
1223.3	
1252.55	
1273	1.7
1295.5	2.0
1322.3	2.1
1352.3	2.9
1375.3	
1391.3	1.8
1418.5	
1437.5	
1453.8	2.3
1474.8	3.0
1504	23.0
1528	6.4
1549.2	3.5
1576	4.6
1598.3	6.2
1619.6	5.2
1643.1	2.7
1669.7	2.9

TABLE A-6

TIME	GAS CHROMATOGRAPH RESULTS EG EFFLUENT (mg/L)				
	(Hrs)	BUCKET	CONTROL	LOW LEVEL NUTRIENT	HIGH LEVEL NUTRIENT
863.3					
1007.3					
1035.8	167.7	162.6	81.8	32.2	
1055.3	171.5	101.6	71.8	17.6	
1082.8	162.7	136.1	23.3	2.2	
1114					
1127.8					
1153.3					
1184.3	255.3	177.2	9.4	5.6	
1208					
1223.3	200.4	178.3	20.8	61.8	
1252.55					
1273	201.9	138.6	1.7	2.9	
1295.5					
1322.3	1800.6	156.6	6.0	3.5	
1352.3					
1375.3	175.6	131.1	11.2	2.1	
1391.3	156.2	125.4	15.9	2.7	
1418.5	161.9	117.6	20.5	1.9	
1437.5	194.4	163.0	25.9	12.0	
1453.8	205.4	168.9	35.5	40.0	
1474.8	208.1	169.0	61.7	26.9	
1504	205.5	154.9	78.3	43.7	
1528	185.0	175.0	80.0	30.9	
1549.2	200.7	195.8	131.9	33.5	
1576	199.6	156.3	161.1	31.0	
1598.3	183.4	169.8	84.1	19.5	
1619.6	196.0	150.9	104.2	19.8	
1643.1	211.6	165.7	104.1	13.7	
1669.7	209.8	162.3	86.3	46.2	
1690.7	196.6	169.5	81.1	27.3	
1719.7	231.6			9.8	
1741.1	207.4			48.8	
1794.7	256.0			48.8	
1838.7	235.6			48.8	
1884.7	233.2		139.8		
1905.7	229.4		60.9		
1929.7	229.8		11.1		
1977.7	196.8			74.6	
1999.2	232.5		45.7	29.3	
2021	214.3		11.8	10.1	
2069	233.2		10.2	7.2	
2120	232.5		44.4	5.4	
2162.5	179.0		34.2	10.3	
2210.5	177.8		67.9	21.9	

TABLE A-7

TIME	% EG REMOVAL		
(Hrs)	CONTROL	LOW LEVEL NUTRIENT	HIGH LEVEL NUTRIENT
1035.80	3	51	81
1055.30	41	58	90
1082.80	16	86	99
1184.30	31	96	98
1223.30	11	90	69
1273.00	31	99	99
1322.30	13	97	98
1375.30	25	94	99
1391.30	20	90	98
1418.50	27	87	99
1437.50	16	87	94
1453.80	18	83	81
1474.80	19	70	87
1504.00	25	62	79
1528.00	5	57	83
1549.20	2	34	83
1576.00	22	19	84
1598.30	7	54	89
1619.60	23	47	90
1643.10	22	51	94
1669.70	23	59	78
1690.70	14	59	86
1719.70			96
1741.10			76
1794.70			81
1838.70			79
1884.70		40	
1905.70		73	
1929.70		95	
1977.70			62
1999.20		80	87
2021.00		95	95
2069.00		96	97
2120.00		81	98
2162.50		81	94
2210.50		62	88

TABLE A-8*Carbon to Nitrogen Ratios*

TIME (Hrs)	C/N LOW-LEVEL NUTRIENT SOURCE	C/N HIGH-LEVEL NUTRIENT SOURCE
1273.00	70	70
1391.30	46	51
1453.80	43	42
1474.80	27	34
1504.00	3	4
1528.00	9	13
1549.20	11	27
1598.30	11	15
1619.60	20	19
1643.10	31	42
1669.70	35	32
1719.70	28	32
Average	28	32