APPLICATION OF OXYGEN MICROBUBBLES FOR *IN SITU* BIODEGRADATION OF P-XYLENE CONTAMINATED GROUND WATER IN A SOIL COLUMN

by

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(ABSTRACT)

In situ biodegradation of p-xylene was studied in a 2.75 inch diameter column using oxygen microbubbles to supply the electron acceptor. One objective was to demonstrate that p-xylene can be biodegraded in the soil column and to follow the degradation and pressure drops as a function of time.

The next objective was to demonstrate the potential for biodegradation of p-xylene in the presence of ferrous iron and to follow bioremediation and anticipated pressure drops as a function of time. Then, an air sparging section was added prior to the biodegradation section to determine if the ferrous iron could be removed in this section. The air sparging section would then be flushed with air and/or water to determine if the ferrous could be removed from the sand matrix and alleviate the expected plugging.

The bacteria degraded p-xylene to below detectable limits until the oxygen supply was exhausted. The pressure drops over this time showed a slight increase over the first

few days and then a gradual decline, which shows promise for *in situ* biodegradation as the microorganisms were thought to cause plugging.

The next run which studied the simultaneous biodegradation of xylene and ferrous oxidation showed no interference from the ferrous iron. The microorganisms seemed to store the oxygen that they needed before the ferrous could oxidize. The pressure drops showed no general trend, therefore the ferric precipitate did not cause an appreciable amount of plugging as expected.

The air sparging section resulted in volatilization of xylene with very little ferrous oxidation. To flush the ferric precipitate from this zone, either a combination of air sparging and backwashing or backwashing at the fluidization velocity was needed to remove the ferric iron.

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CHAPTER 1

INTRODUCTION

As the environmental movement gains momentum, concern is directed toward the quality of our water resources. Currently, 25% of the world's water usage is supplied from ground water, and 50% of the world population uses ground water as its source of drinking water (Lehr 1987). Contamination of ground water is occurring more and more frequently due to unintentional losses of manmade chemicals. The United States Environmental Protection Agency estimated that trichloroethylene has contaminated 4% of the nation's groundwater supply (Anon. 1984).

In situ biodegradation, which has been gaining interest over the past fifteen years, is a remediation technique which can be used to treat contamination in the saturated zone. Several other soil and groundwater remediation methods exist and will be discussed later.

In situ biodegradation would be most suited at a site where the contaminant can be aerobically biodegraded, since the rates are generally faster than anaerobic degradation (McCarty 1987). With *in situ* biodegradation, indigenous or introduced microorganisms would be encouraged to grow in the subsurface, where the microbe can utilize the contaminant in its respiration process. The addition of

nutrients and an electron acceptor, which is usually oxygen may also be required for biodegradation to occur.

In order for *in situ* aerobic biodegradation to take place, oxygen must be added to the ground water, since most ground water has a low dissolved oxygen concentration. Oxygen transfer can be accomplished by several methods in pilot-scale testing, such as air or oxygen sparging, oxygenated water injection, hydrogen peroxide addition, or oxygen microbubble injection. Previous pilot scale testing has shown promise for oxygen microbubbles. They have proven to be more effective than air sparging, oxygenated water, and hydrogen peroxide in transferring oxygen to ground water with a low dissolved oxygen concentration (Lotfi 1990) (Achanta 1991). Pilot scale testing in a 7'x 7'x 5" test cell has produced oxygen utilization of up to 59% using oxygen microbubbles (Lotfi 1990). These results show promise for microbubbles and suggest that they could be the optimum method for oxygen transfer to ground water.

In situ aerobic biodegradation of glucose has also been studied at small pilot scale to determine the feasibility of using microbubbles and to determine the effect that ferrous iron in the ground water has on the degradation process (Achanta 1991). Results from this research indicate that glucose can be biodegraded using microbubbles, and that the presence of ferrous causes

complications, as the ferrous oxidation consumes the oxygen before the glucose biodegradation can. Also, both the glucose biodegradation process and the ferric precipitation result in plugging of the soil matrix.

One recommendation from this research was to oxidize the ferrous iron before the ground water reaches the area of biodegradation and to attempt to remove the ferric precipitate by backwashing to reduce pressure drops. The other recommendation was to study biodegradation of a contaminant that would be present in a contaminated aquifer such as a petroleum hydrocarbon. The pseudomonas type bacteria that degrade hydrocarbons are much smaller than the glucose degrading organism used in the previous research, so less plugging should result from the microorganism presence.

Therefore, this research studied *in situ* biodegradation of p-xylene in flowing ground water using a soil column to simulate a treatment trench. P-xylene was been chosen as the contaminant, since it is a petroleum hydrocarbon which can be aerobically biodegraded and is found at many contaminated sites where a fuel spillage has occurred.

The first objective of this work was to prove that no xylene was lost to volatilization or adsorption through the chosen system. Once this was done, any reduction in xylene concentration could be attributed to biodegradation. The

second objective was to demonstrate that xylene can be aerobically biodegraded in the soil column and to follow the degradation and pressure drops as a function of time. Oxygen microbubbles were intermittently injected into the bioremediation treatment zone to provide the electron acceptor for degradation. Influent and effluent xylene and oxygen concentrations were measured in order to determine the amount of oxygen utilized.

The third objective was to demonstrate the potential for biodegradation of xylene in the presence of ferrous iron and to follow bioremediation and anticipated pressure drops as a function of time. To fulfill the fourth objective, an air bubbling section was added prior to the biodegradation zone at the top of the column. Then, a solution of ferrous iron and xylene was fed to the column to determine if the air bubbling section was effective in oxidizing the ferrous iron before the ground water reached the biodegradation area. Some volatilization of xylene was also expected. The fifth objective was to attempt to remove the ferric precipitate from the air sparging zone by backwashing to reduce expected pressure drops. The final objective was to provide direction for design of future laboratory, pilot, and field testing determined by results obtained from this work.

CHAPTER 2

LITERATURE REVIEW AND BACKGROUND

2.1 Soil and Groundwater Remediation Techniques

Contamination of soil and ground water is occurring more and more frequently. Various treatment technologies can be applied to contaminated soil and ground water. If the contaminant is adsorbed on the soil particles and immobilized, or if natural biodegradation occurs, then no remedial action would be required.

Barriers can be used to contain contaminated ground water and prevent it from further contaminating the aquifer. The barriers can be placed either upstream from the contaminated site to reduce flow of uncontaminated ground water through the spillage, or downstream to reduce contaminant migration. These barriers consist of a low permeability material which replaces the soil in the subsurface (displacement walls).

Traditionally, pumping the ground water from the subsurface and treating it above ground has been used as a remediation technique. The treated water may have to be discharged to a publicly owned treatment work or, if the regulations allow it, reinjected into the ground. By using a combination of pumping and injection wells, a hydraulic

barrier could be created (Thomson 1990). However, pump and treat methods generally take a long time, and determining when the site is clean is difficult.

In some cases, excavation of the soil is required to remediate contamination in the subsurface. The soil may either be treated above ground or landfilled which is costly. Removal of the ground water by pumping may also be required to completely remediate the site.

Thomson et al. discusses permeable barriers for treating contaminated ground water (1990). Two types of barriers could be used depending on the aquifer location. For a deep contaminated aquifer, a well based barrier would need to be used in which the contamination was altered chemically but not hydraulically. For a shallow aquifer (<20 m), a trench based barrier could be placed downstream from the contamination zone. The trench would contain activated carbon, ion exchange media, or microbial growth media to enhance biodegradation. A chemical precipitation or addition system could be implemented to neutralize acidic ground water for example.

Soil venting is another option if the contamination lies within the unsaturated zone and is volatile. Soil venting or soil vapor extraction uses a negative pressure source to remove the volatile organic from the soil matrix as a vapor.

The vapor is then captured and treated usually using activated carbon.

Air sparging is a relatively new treatment technology and can be applied if the contaminant is volatile and lies in the saturated zone. With air sparging, a porous bubbler device is positioned below the water table. Air under pressure is sparged through soils below the water table. This process removes contaminants that are adsorbed on the soil particles and dissolved in the water phase. The vapors most likely will have to be treated, possibly by using a soil vapor extraction system in conjunction with air sparging. Angell (1991) described two case studies in which air sparging was successfully applied in the field. Both soil venting and air sparging increase the air flow through the subsurface thus increasing the oxygen level which in turn will stimulate natural biodegradation.

However, a low permeability barrier, consisting of clay for example, above the potential area of air injection, would reduce effectiveness of air sparging. Also if the geology of the site prohibits vertical air flow, then the contamination may spread concentrically from the air injection point. If either of these conditions exist in a potential air sparging remediation zone, then a ground water recovery system would be required to prevent further spread of contamination (Angell 1991).

However, a site with either one of these subsurface characteristics would be ideal for in situ biodegradation using oxygen microbubbles. The natural clay barrier would prevent the oxygen source from escaping and increase utilization. The site geology, mentioned previously, would induce flow of the oxygen source to areas of contamination rather than to the surface. Caution would need to be taken not to spread the contaminant to clean areas.

One major advantage of *in situ* biodegradation is that the contaminant is converted to innocuous end products. The regulatory agencies are moving toward biodegradation in general as a treatment technology (Thayer 1991). Also, handling of the contamination and excavation which is costly are not required with *in situ* biodegradation. In many cases, *in situ* biodegradation can be the most cost effective treatment depending on the site characteristics.

However, determining when the contaminated site is clean can be difficult with in situ biodegradation. Another disadvantage is the long period of time it takes to remediate a site. Because of the uncontrollability in field studies of in situ biodegradation, identifying that contaminant loss is due to biodegradation can be difficult (Madsen 1991). Madsen proposes a stepwise strategy for determining in situ biodegradation processes in a field situation.

Research conducted at Virginia Tech has studied injection and retention of oxygen microbubbles in the saturated zone of a pilot scale vertical slice test cell as well as the transfer of oxygen to the flowing ground water (Michelsen, Lotfi 1990). These tests have led to a proposed field scenario for *in situ* biodegradation of contaminated ground water. Alternate layering of coarse concrete sand and clay in the treatment trench directs ground water flow through the coarse sand layers. The coarse sand layers contain degrading microorganisms, nutrients, and oxygen microbubbles. The clay layers help to retain the oxygen in the saturated zone which increases the oxygen retention and transfer to the flowing ground water.

Pilot-scale research has also studied the introduction of oxygen microbubbles to soil using a fork like probe for contamination in a sediment pond (Michelsen et al. 1984). In tests, a three-prong "fork" would plow through the sand matrix while injecting microbubbles. Results from these tests indicate that a faster plow rate and slower CGA delivery rate contribute to a higher percentage of gas retention.

2.2 Microbubbles

Laboratory scale research at Virginia Tech has studied the use of oxygen microbubbles for biodegradation of organics compounds as well as for fine particular and biological matter (Michelsen et al. 1984, 1985, 1988). Microbubbles, also termed colloidal gas aphrons (CGA) by Sebba (1987), are defined as "a collection of spherical, micron-sized gas bubbles dispersed in an aqueous surfactant solution with a volumetric gas fraction (quality) of at most 0.74 and 95% of its bubbles not exceeding 100 microns in diameters" (Longe 1989). Since microbubbles are defined to be less than 74% gas, they are placed in the wet category of foams. Dry foams cannot be transferred through a tube using a pressurized generator and still retain their foam characteristics. Microbubbles flow as easily as water, which gives them many applications, and can be transferred using some positive displacement pumps but neither ball valve positive displacement pumps nor centrifugal pumps.

The bubble diameters of wet foams can vary widely and depend on the generation technique, surfactant type and concentration, and the characteristics of the water. When the bubble diameters are less than 250 microns the foam is more stable than if the diameters were greater than 250 microns. The foam shows colloidal properties as the bubble

diameter is reduced to 50 microns or smaller with few greater than 100 microns (Longe 1989). One colloidal property exhibited by the foam is that the bubbles rarely coalesce as long as they are completely immersed in water. Sebba (1986) gives a bubble diameter range of 25 to 50 microns, while Longe (1989) gives a range of 15 to 120 microns with an average diameter of 50.7 ± 22.7 microns.

Microbubbles can be readily characterized by two parameters, quality and stability (Michelsen 1990). Quality (Q) is defined as the percent of gas in a gas plus water dispersion. A quality between 60 and 70% is usually desired. Stability (H') is the volume of clear liquid in one minute after pouring the dispersion into a 250 ml PET graduated cylinder. So, the smaller the clear liquid volume is, the more stable the dispersion is. Stability (H) is defined as the percent of the total liquid volume coalesced in one minute. These parameters can be determined easily by filling a 250 ml graduated cylinder with microbubbles, weighing it, and measuring the clear liquid volume at the bottom after one minute. Earlier published data used a 250 ml glass graduated cylinder which would have given better stability values (lower clear liquid volume) than measured in this study. Other parameters that characterize microbubbles include viscosity and microscopic determination of size.

Microbubbles can be made using a bench scale spinning disk generator. A surfactant is added to water to attain a concentration of 100 to 200 ppm. The surfactant lowers the surface tension of the water and enables the bubble to remain immersed. The spinning disk shears the water against the baffle and imparts gas into the liquid phase. This method was first described by Sebba (1985) and later scaled-up by Michelsen et al. (1988). The details of the large scale generator are not discussed here, as the process is undergoing patent proceedings.

The use of oxygen microbubbles for groundwater oxygenation has several advantages. The microbubbles can maintain their integrity for long periods of time (Michelsen 1984). The injected microbubbles form a cloud around the injector port through which the ground water passes and gradually picks up the oxygen (Lotfi 1990). Through several studies, oxygen microbubbles have proven to be more efficient in transferring oxygen to the liquid phase than other modes such as air sparging, hydrogen peroxide addition, and oxygenated water injection (Lotfi 1990) (Achanta 1991).

However, the use of microbubbles also has disadvantages. The cost of microbubble generation is more than air sparging but less than hydrogen peroxide injection (Michelsen et al. 1990). Also, introduction of the surfactant to the subsurface places another demand on the dissolved oxygen.

The surfactant biodegradation will consume 14% of the injected oxygen for a 150 ppm surfactant solution which consists of 75% Tergitol 15-S-12 (Union-Carbide) and 25% Sodium Dodecyl Benzene Sulfonate (calculation can be found in Appendix B). The use of pure oxygen also requires careful handling since it can cause ignitions easily.

The use of air microbubbles for flotation of particulates and biological matter such as phosphate slime, algae, and coal has been studied on a laboratory scale (Honeycutt et al. 1983) (Sebba, Yoon 1982). Also, air microbubbles have proven to be more effective in supplying oxygen for yeast fermentation than air sparging in laboratory tests (Kaster et al. 1990).

CGA with methane gas in the core of the bubble has been proposed for co-metabolism by methanotrophs of halogenated hydrocarbon solvents such as tetrachloroethylene and trichloroethylene which are resistant to aerobic biodegradation.

2.3 Vertical Slice Test Cell

Pilot-scale tests have been used to study the injection of oxygen microbubbles into a soil matrix and the resulting transfer of oxygen to the flowing ground water (Michelsen et

al. 1990). Much of this research has been performed on a Vertical Slice Test Cell (VSTC) and various Vertical Column Test Cells (VCTC) which are discussed elsewhere (Michelsen 1990) (Lotfi 1990). The VSTC, which is 7 feet by 7 feet and 5 inches deep, has been tested recently after charging with alternate layers of concrete sand and clay. The impermeable clay layer serves to direct the groundwater flow through the coarse sand layer into which the microbubbles are injected. The clay layer should help retain the microbubbles in the coarse sand layer and keep them from rising to the unsaturated zone, thereby increasing the transfer of oxygen to the ground water.

Experiments were conducted to improve gas retention and increase the efficiency of oxygen transfer to the water phase (Lotfi 1990). In these experiments, the initial gas hold-up, the percent of oxygen transferred to the ground water, and the oxygen transfer coefficient were calculated to compare microbubble injection tests. Studies were also performed to compare oxygen microbubbles to air sparging and oxygenated water as means of transferring oxygen to ground water.

Several valuable conclusions were obtained from this research. High quality and stability of microbubbles increased the oxygen retention, transfer, and mass transfer coefficient while low quality and stability adversely affected these parameters.

Oxygen microbubbles were more efficient in transferring oxygen to the ground water than air sparging or oxygenated water injection. Between 29 and 59% of injected oxygen was transferred to the flowing ground water during this testing.

The oxygen mass transfer coefficient was highest when the cell was overloaded with microbubbles. However, the retention and percent of oxygen transferred were highest when the holdup capacity was not exceeded. Oxygen microbubble injections yielded higher mass transfer coefficients than oxygenated water injection and lower mass transfer coefficients than air sparging.

The mass transfer coefficient for a packed bed has been defined as follows (Treybal 1980):

$$L\ (X_2-X_1) = K_1a\ Z\ (X_A - X_{A,L}) \qquad (1)$$

$$K_1a = \frac{L\ (X_2-X_1)}{Z\ (X_A - X_{A,L})} \qquad (2)$$

where: Kla = mass transfer coefficient (hr-1)

$$\text{or} = \frac{\frac{mg}{l\ hr}\ O_2 \text{ dissolved in liquid phase}}{\frac{mg}{l}\ O_2 \text{ driving force}}$$

L = flow velocity (Q/A) (cm/hr)

X_2= effluent DO (mg/l)

X_1= influent DO (mg/l)

Z = mass transfer zone (cm)

$X_A - X_{A,L}$ = log mean driving force

$$= \frac{(C_s-X_1) - (C_s-X_2)}{\ln \frac{C_s-X_1}{C_s-X_2}} \qquad (3)$$

C_s = Saturation conc.of O_2 in water (mg/l)

The left side of the equation represents the amount of oxygen dissolved in the flowing ground water, utilized for xylene biodegradation and utilized for ferrous oxidation. The mass transfer zone (Z), as shown in Figure 1, is the length of the column along which mass transfer of oxygen was occurring. The log mean driving force is an averaged oxygen concentration in the saturated zone. The Kla for active air sparging and oxygen transfer to ground water may be higher than for transfer from quiescent oxygen microbubbles to flowing ground water. However, the (C_s-X_1) cannot be above 9 mg/l for sparging air, but it can be 35 to 45 mg/l for pure oxygen microbubbles. Thus, typically the mg of O_2 transferred/(l hr) is higher for oxygen microbubbles than with air sparging which may be a better indication of the mass transfer of oxygen.

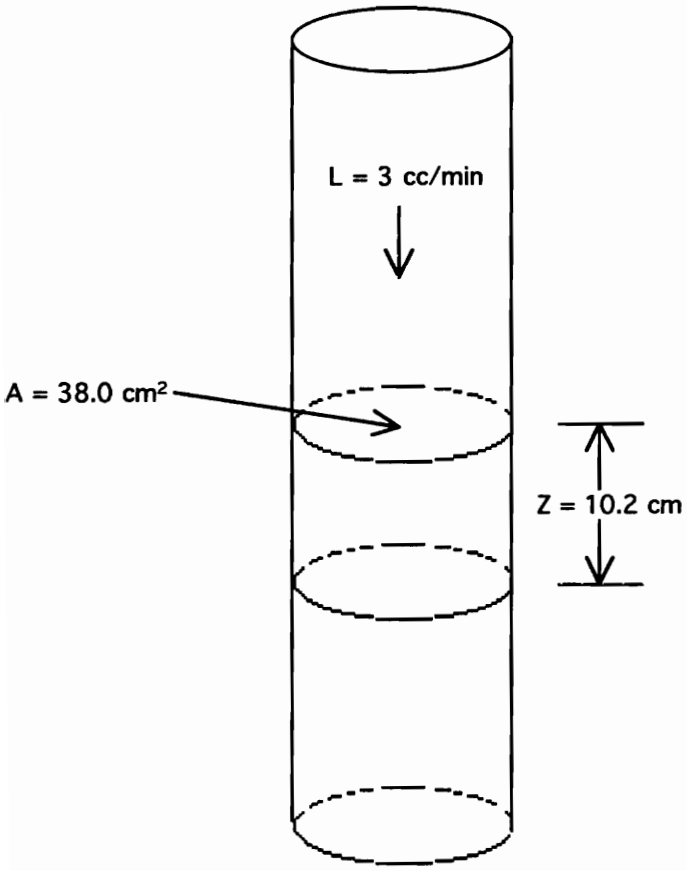

Figure 1: Mass Transfer Model for Vertical Column Test Cell

2.4 Biological Activity

The transfer of oxygen from microbubbles to flowing ground water for *in situ* biodegradation of contaminated ground water has been studied extensively at the pilot scale. This research has led to *in situ* biodegradation of a contaminant at the small pilot scale. With *in situ* bioremediation, microorganisms within the subsurface utilize the contaminant in their respiration process. When a contaminant enters the subsurface, bacteria which can utilize the contaminant will dominate the microbial population. The subsurface has an estimated bacterial population of ten million organisms per gram of dry soil.

When the microbe oxidizes the contaminant, another chemical species must serve as the electron acceptor. When this electron acceptor is oxygen the process is termed aerobic respiration. Some groundwater aquifers with shallow water tables may have high dissolved oxygen concentrations, but many aquifers have concentrations of dissolved oxygen below one part per million. Many organic contaminants can be anaerobically biodegraded, but it generally takes one to two orders of magnitude longer (Rainwater 1989). Since petroleum hydrocarbons are biodegraded faster aerobically, aerobic biodegradation will be discussed here.

For *in situ* aerobic respiration to occur, several components must be present in the subsurface. First, the microorganism that uses the contaminant as a substrate must be present. If an indigenous microorganism is not present, then bacteria that will biodegrade the contaminant must be introduced. How the introduced bacteria will interact with the indigenous microorganisms is not known yet.

The bacteria need nutrients and oxygen for aerobic respiration to take place. Microorganisms need a relatively small amount of nutrients to thrive, which can be introduced using injections of the nutrient solution. Therefore, the primary objective of *in situ* bioremediation is transferring oxygen effectively and efficiently in order to support the microbial respiration process.

Oxygen transfer can be performed in several ways such as air sparging or hydrogen peroxide addition, which have been performed in the field, and air or oxygen microbubble injection on a pilot scale test cell. With air sparging, compressed air is pumped through a porous bubbler device which is positioned below the water table. The maximum interfacial oxygen concentration is limited to 8 to 12 mg/l of oxygen. Oxygen sparging can attain interfacial oxygen concentrations of 40 to 50 mg/l. One problem with the sparging process is that portions of gas tend to clog parts of the soil matrix and limit groundwater flow through that

area (Rainwater 1989). The use of pure oxygen also requires careful handling. While hydrogen peroxide injections to the ground water can attain high dissolved oxygen levels, extremely high levels of dissolved oxygen can be toxic to the degrading microorganisms. Also, hydrogen peroxide has been found to decompose due to a bacterial catalase (Spain 1989). Also extremely high levels of dissolved oxygen can be toxic to the degrading microorganisms. Oxygen microbubbles have shown promise over these methods in transferring oxygen to ground water, as discussed in section 2.2.

2.5 Glucose Biodegradation

Another group of tests were performed which studied *in situ* biodegradation of glucose (Achanta 1991). The purpose of this research was to determine the extent of plugging caused by biodegradation and ferric hydroxide precipitation and to determine the effectiveness of biodegradation in the presence of ferrous iron. This work also compared biodegradation using oxygen microbubble injections and hydrogen peroxide injections.

Glucose was chosen as the substrate since it can be aerobically biodegraded, and it is easier to handle than petroleum hydrocarbons. Tests were performed on a 1.5 inch

diameter column with flow rates between 2.1 and 4.5 ml/min which corresponds to 22 to 47 ft/day, which are high flow rates for ground water, since typical flow rates are in the range of 3 to 6 ft/day.

One objective of this research was to compare biodegradation using hydrogen peroxide as the oxygen source to biodegradation using oxygen microbubbles as the oxygen source. In all tests the same amount of oxygen was injected. However, during oxygen microbubble injections, the microorganisms biodegraded more glucose than during hydrogen peroxide addition which is attributed to the instability of hydrogen peroxide.

Another aspect of this testing considered the presence of ferrous iron in the ground water. Solutions containing glucose and varying concentrations of ferrous iron were fed to the column. The ferrous oxidation took precedence over the biodegradation process, as the microorganisms fully biodegraded the glucose only when the ferrous concentration was low. Also head losses of up to 15 inches were obtained in this research. These results indicate that a method for removing the ferrous iron prior to the biodegradation zone and a means of flushing the ferric precipitate out of the subsurface would be desirable in order for *in situ* biodegradation to occur.

Cunningham et al. (1991) studied the influence of biofilm accumulation on media porosity, permeability, and friction factor using laboratory scale biofilm reactors. Glucose was chosen as the substrate in this work also. The reactors used in this experiment were five centimeters in length and three layers of media thick. The media in the four reactors consisted of 1 mm glass spheres, 0.70 mm sand, 0.54 mm sand, and 0.12 mm glass and sand. *Pseudomonas aeruginosa* was used as the innoculum because it forms a very uniform biofilm which facilitates measurement of film thickness on porous media particles.

Results from this study showed that the biofilm thickness increased from the start of the experiment until approximately the fifth day when a quasi-steady-state thickness was reached. Several interactions cause this steady state. As the biofilm thickness on the media increases, the nutrients are less likely to reach the base of the film. Also, under constant piezometric head gradient, the increased biofilm thickness will also decrease the pore velocity which will reduce transport of nutrients to the film-water interface which results in a reduction of biofilm growth. The decreased pore velocities will also reduce the shear stress which in turn reduces the detachment rate. Biofilm growth will occur until the specific growth rate is balanced by detachment rate.

Once the biofilm thickness reaches steady state, the permeability stabilizes and remains constant between 1 and 5% of the original clean surface permeability regardless of the media particle diameter. This result suggests that, in this research, the biofilm accumulation process stabilizes in order to preserve a minimum permeability within the porous media reactor.

When the pore space is reduced due to biofilm accumulation, the media porosity and permeability will decrease which corresponds to an increase in the friction factor. A strong correlation between these variables was observed in this work and can be used to predict certain variables knowing only one parameter. For example, if the biofilm thickness could be measured or calculated based on kinetic parameters, estimates of porosity, permeability, and the friction factor could be made from relationships determined in this research.

CHAPTER 3

EXPERIMENTAL METHOD

3.1 Objectives

As contaminants pollute the ground water more and more frequently, there is a growing need for a technology to remove these contaminants effectively and efficiently. *In situ* biodegradation can be a viable option for groundwater remediation when the degrading bacteria, nutrients, and electron acceptor are present in the subsurface. Previously, *in situ* biodegradation of glucose using microbubbles to supply the oxygen was studied. Therefore, the next step was to study biodegradation of a petroleum hydrocarbon frequently found in contaminated ground water, therefore this research studied *in situ* biodegradation of para-xylene. It is present in many ground waters where a petroleum spillage has occurred, and it can readily be aerobically biodegraded. P-xylene is also a non-priority pollutant, whereas benzene and toluene are priority pollutants. However, future research should study biodegradation of a mixture of contaminants in order to determine how the various degrading microorganisms will interact.

The first objective of this work was to prove that no p-xylene was lost to volatilization or adsorption through the chosen system. Once proven, any reduction in p-xylene concentration could be attributed to biodegradation. The second objective was to demonstrate that p-xylene can be aerobically biodegraded in the soil column and to follow the degradation and pressure drops as a function of time. Oxygen microbubbles were intermittently injected into the bioremediation treatment zone to provide the electron acceptor for degradation. Microbubbles were not reinjected until the oxygen supply was exhausted. A material balance was performed on the oxygen.

The material balance was performed around the whole column for xylene biodegradation tests. The xylene concentration entering and leaving the column was monitored. The microorganisms were assumed to biodegrade the difference. Stoichiometrically, one ppm xylene requires 3.2 ppm oxygen for oxidation, therefore this factor was used in calculating the amount of oxygen that contributed to biodegradation (all calculations can be found in Appendix B). However, McCarty includes the cell synthesis equation when discussing biodegradation (McCarty 1988). By including this equation some of the contaminant will contribute to new cell formation and will therefore lessen the demand on the oxygen.

The dissolved oxygen concentration was also monitored entering and leaving the column. The difference was the amount of oxygen transferred to ground water from the injected microbubbles. For a quality of 65% and a 150 ppm surfactant solution, the surfactant biodegradation will require 14% of the injected oxygen in order to biodegrade. In determining the material balance, the surfactant was assumed to have been completely biodegraded. The microbubbles can be generated using a 125 ppm surfactant solution which would lessen the injected oxygen demand.

The third objective was to demonstrate the potential for biodegradation of p-xylene in the presence of ferrous iron and to follow bioremediation and anticipated pressure drops as a function of time.

The same assumptions mentioned previously were used for the material balance. The ferrous concentrations were measured entering and leaving the column, and the difference was assumed to be oxidized by the injected microbubbles. Stoichiometrically, 1 ppm oxygen oxidizes 7 ppm ferrous iron, so this ratio was used in calculating the amount of oxygen oxidizing the ferrous (calculation can be found in Appendix B).

The fourth objective was to demonstrate the effectiveness of removing the ferrous iron prior to the biodegradation zone. Either air or aerated water was added

prior to the bioremediation zone to determine if the ferrous iron can be precipitated inexpensively before the ground water reaches the microorganisms. Then, this ferrous removal zone was flushed with water or a combination of air and water to determine if the ferric precipitate could be removed to reduce expected pressure drops.

The same assumptions were used in calculating the material balance for the fourth objective. In addition to the influent and effluent concentrations, the xylene and ferrous concentrations were measured after the air sparging zone/before biodegradation zone to determine the concentrations oxidized and volatilized in the air sparging zone and the concentrations oxidized and biodegraded in the biodegradation zone.

The fifth objective was to flush the ferric hydroxide precipitate out of the air sparging zone. The sixth objective was to provide direction for future research of *in situ* biodegradation.

3.2 Equipment Design and Operations

To fulfill the first objective, the feed system, as shown in Figure 2, was designed to contain the p-xylene so

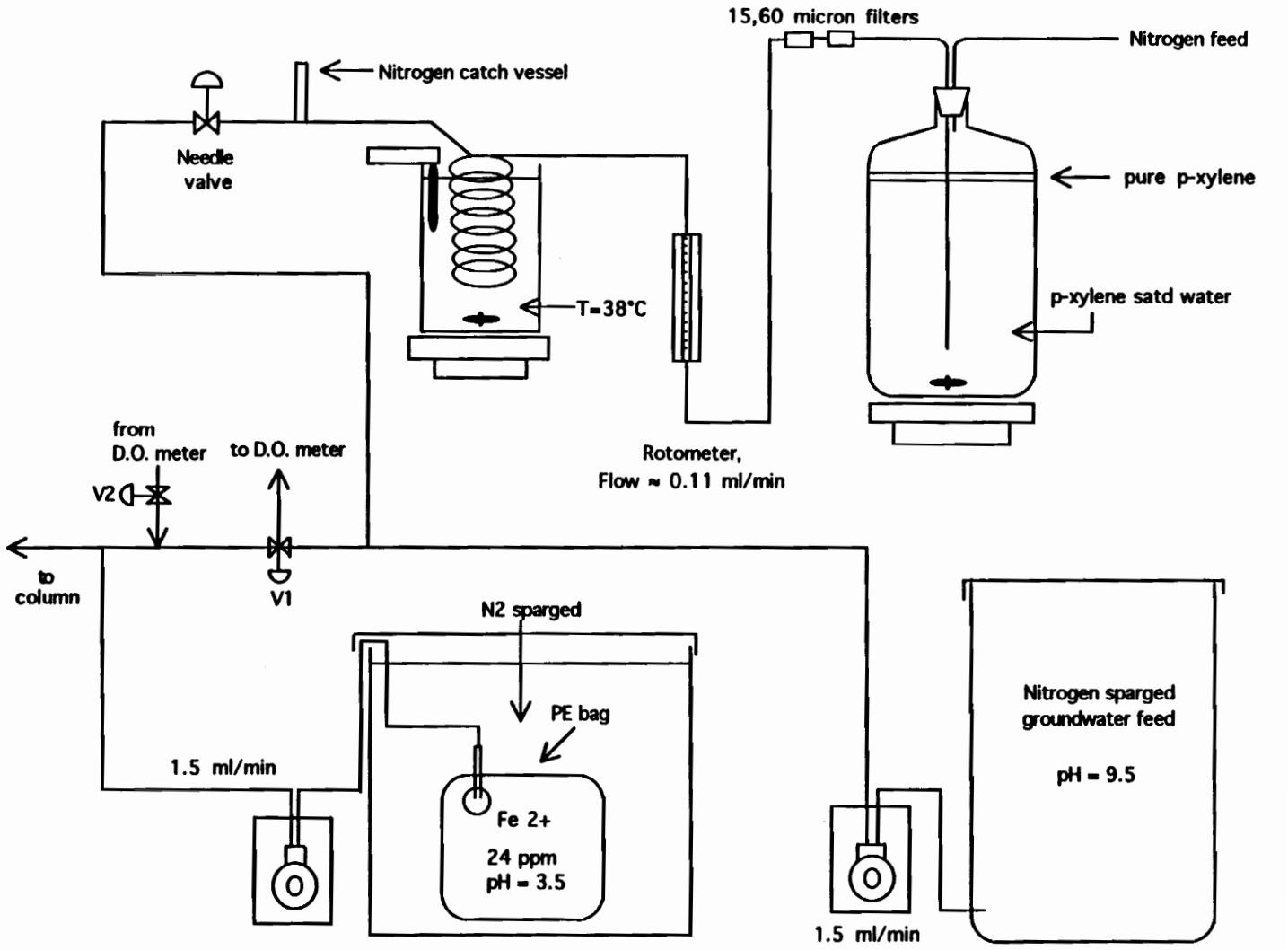

Figure 2: Feed System for Vertical Column Test Cell

that none was lost to volatilization or adsorption. The p-xylene saturated water with pure xylene layer was stirred for several days to insure that the water was saturated before being used as the feed. Water saturated with p-xylene contains 200 ppm at room temperature according to Lange's Handbook of Chemistry (1985) or 198 ppm at 25°C (Handbook of Environmental Data, 1983). The temperature of the saturated solution used in the experiment was approximately room temperature. However, since the room temperature did vary, there is some error in the saturation concentration. The degree of the error is not known. Since the difference in the influent and effluent xylene concentrations was used in calculating the oxygen utilization, error in saturation concentration should have a small effect on the overall oxygen utilization.

Teflon tubing was used in all streams containing p-xylene to reduce the amount adsorbed in the tubing. Two filters, 15 and 60 micron, were placed in-line to remove any fine particulates and to prevent the 0.1 ml/min rotometer from becoming partially plugged. The water was heated to purge out dissolved nitrogen gas from solution in order to prevent any nitrogen from forming bubbles and partially blocking flow through the needle valve which controlled the xylene flow. The concentrated solution was diluted to 6 to 7 ppm p-xylene.

The ferrous solution was stored in a polyethylene (PE) bag that was submerged in low dissolved oxygen (DO) water to prevent oxygen from permeating through the PE bag and oxidizing the iron. The ferrous solution pH was lowered to 3.5 since ferrous is more soluble at lower pH values. The groundwater pH was at 9.5, so that a neutral pH was attained when the two streams mixed. The pH of the effluent stream was measured periodically during tests where ferrous iron was present in the ground water. The optimum pH for biodegradation is 6.

The groundwater feed was continuously sparged with nitrogen to maintain a dissolved oxygen concentration less than 1 mg/l. In tests where ferrous iron was not present in the feed stream, the groundwater pump transferred the feed at a rate of 3 ml/min. In other tests, the ferrous feed stream pump and the groundwater feed stream pump flowed at 1.5 ml/min each.

The configuration of the polycarbonate column in Figure 3 was used for all tests except air sparging tests. Polycarbonate offers the advantage of being transparent as opposed to stainless steel. Polycarbonate is also easier to drill ports in than glass and is not as fragile.

The p-xylene degrading microorganisms, *Pseudomonas Putida*, were obtained from Envirotech Mid-Atlantic located in the Corporate Research Center at Virginia Polytechnic

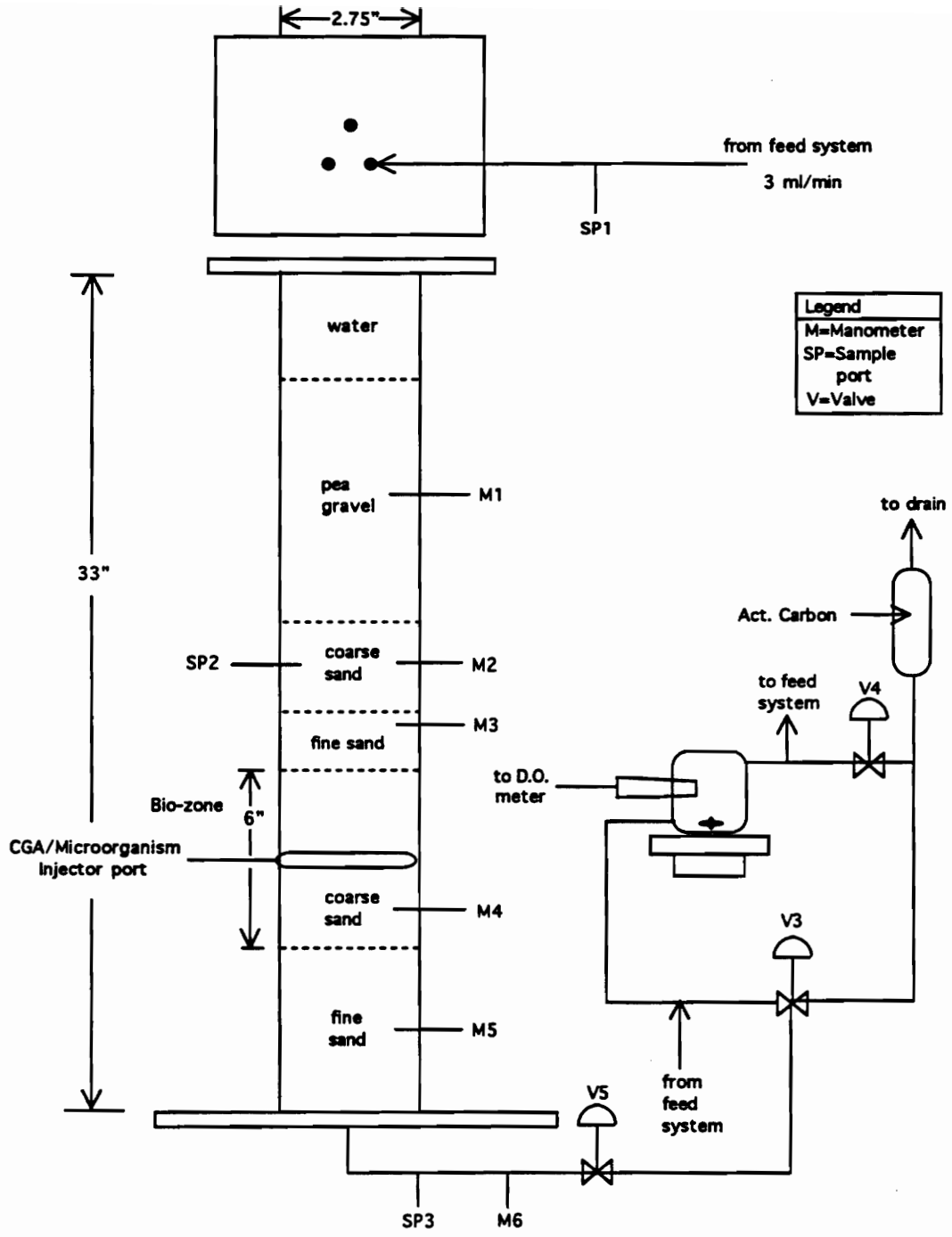

Figure 3: Vertical Column Test Cell

Institute and State University. The *Pseudomonas* type bacteria is a good choice as three different *Pseudomonas* bacteria have been known to degrade diesel fuel, however the *Achromobacter* strain has also degraded diesel fuel (Tasker 1988). The bacteria were observed under a microscope and estimated to be 0.5 μm wide and between 1 and 2 μm in length.

New microorganism cultures were started periodically by adding 1 ml of the most recently cultured bacteria solution to 100 ml of growth media and adding p-xylene to attain 500 ppm. The solution agitated constantly on a shaker table. The rubber stoppers were removed from the glass flasks approximately once a week to replace the air. The contents of the growth media are listed in Tables 1 and 2. During the experiment 10 to 15 milliliters of the growth media were injected into the column through SP2 daily to supply the microorganisms with nutrients.

3.3 Sampling Protocol and Analysis

A diagram of the sample port used in the experiment is pictured on Figure 4. The sample ports were packed with glass wool to minimize the void volume. Samples were obtained using a syringe with a female luer lock end and

Table 1

Minimal Salts Media Composition

Compound	Amount
KH_2PO_4	3.8 g/l
K_2HPO_4	12.5 g/l
$(NH_4)_2HPO_4$	1 g/l
Trace Minerals	1 ml/l

Table 2

Trace Minerals Solution

Compound	Amount (g/100ml)
$MgSO_4$	4.0
NaCl	0.2
$FeSO_4 \cdot 7H_2O$	0.2
$MnSO_4 \cdot H_2O$	0.2
$CaCl_2 \cdot 2H_2O$	0.2

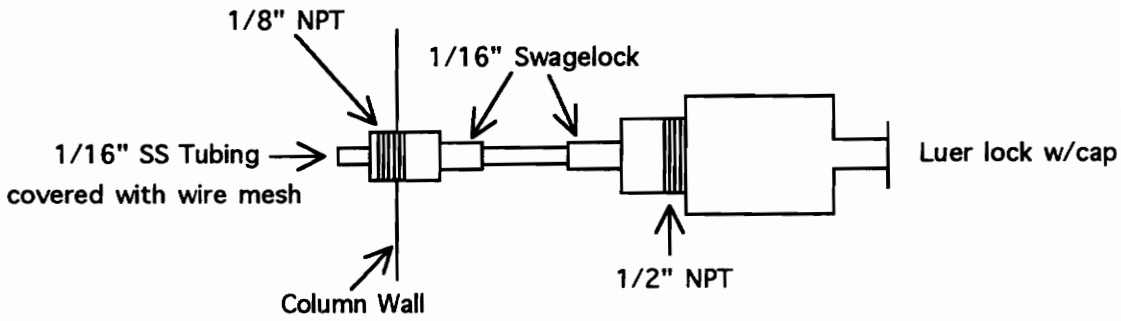

Figure 4: Sample Port Configuration

placed in an eight milliliter sample vial, with no head space to minimize volatilization. The sample was taken over three minutes to minimize disruption of the system, since the water flow rate was only 3 ml/min.

Eight milliliters of sample were taken in case a purge and trap gas chromatograph analysis was required which demands 5 ml of sample. However, due to time constraints only direct inject analysis was performed which requires only 2 μl of sample. Therefore, a smaller sample volume could have been taken.

Sodium azide was used to preserve the samples at a concentration of 0.55 g/l when only p-xylene analysis was performed. When the ferrous analyzation was performed, the samples were preserved with concentrated hydrochloric acid to attain a pH of 1.5. The vials were sealed with an open top cap and Teflon faced silicone septum and then refrigerated.

As seen in Figure 3, to measure the dissolved oxygen (DO), the stream was directed through a 30 ml plexiglass chamber with a DO probe positioned in the side. The chamber contained a magnetic stir bar and was placed on a stirrer plate. The valves could be maneuvered so that either the influent stream, effluent stream, or neither was being measured for dissolved oxygen. The membrane on the DO probe was changed, and the meter was calibrated

approximately every two weeks as algae would grow on the membrane. A DO microprobe placed directly in the area of biodegradation would be beneficial to determine how the oxygen is being utilized better.

The DO meter was checked against the Winkler titration method twice during the experiment (Standard Methods 1989). A calibrated meter reading of a tap water sample was 7.4 mg/l which corresponded to a value of 7.9 mg/l using the Winkler method. A second sample containing 3.8 mg/l oxygen, according to the DO meter, had 3.3 mg/l using the Winkler method. If each effluent dissolved oxygen reading was 0.5 mg/l lower than the actual amount, an approximate 3% increase in the overall oxygen utilization would result.

The samples were analyzed for p-xylene using a Hewlett-Packard 5710A gas chromatograph. The column was packed with Carbopack FTA and operated at a column temperature of 170°C. P-xylene saturated water at room temperature was diluted to 5 and 10 ppm. Three samples of each concentration were stored in glass vials and sealed with Teflon faced septa and open top caps. Standards were prepared prior to analyzing samples and were injected at beginning, middle, and end of sample analyzation.

Samples were analyzed for ferrous iron using a colorimetric procedure with bathophenanthroline (Lee 1960). This procedure is more reliable according to Lee than the

procedure using 1,10-phenanthroline in Standard Methods (1989). One advantage of this procedure is that bathophenanthroline is two times more sensitive than 1,10-phenanthroline. The Standard Methods procedure is unreliable for concentrations below 1 ppm and is susceptible to inferences. The red ferrous bathophenanthroline complex is extracted using *n*-hexyl alcohol which renders the procedure less subject to interferences. The procedure could detect as low as 0.5 μg of ferrous iron using a spectrophotometer with a 1 cm light path.

3.4 Operating Procedure

Throughout the experiment, readings were taken four times a day at approximately 9:00 am, 2:00 pm, 7:00 pm, and 12:00 am. Readings consisted of taking influent (SP1), pre-biozone (SP2) and/or effluent (SP3) samples, recording manometer levels, measuring effluent DO, and measuring effluent flow rate. Manometer levels were recorded by way of piezometers connected along the back face of the column. The influent dissolved oxygen concentration was measured approximately once a week since it remained relatively constant. Effluent pH was measured 2 or 3 times a week

when ferrous was present in the feed. Vent losses were determined by replacing the oxygen bubble at the top of the column with a known volume of the minimal salt media solution using a graduated hypodermic needle.

To fulfill the first objective (I), an 8 ppm solution of p-xylene was fed to the column at 5 ml/min until steady state was reached with respect to xylene concentration. Data for the run (I-0) and all other raw data can be found in Appendix A. After steady state was reached, any reduction in xylene concentration could be attributed to biodegradation.

In order to prove the second objective (II), a seven day old bacteria culture was injected in the column. At seven days old the culture is in the log growth phase and should flourish in the column. The culture was analyzed for xylene before injecting because a high concentration of xylene would cause an error in the material balance.

Approximately 125 mg of oxygen corresponding to 192 ml of CGA with a 65% quality were introduced into the column following the microorganism injection. In all microbubble injections, the pumps to the column were stopped and the three way valve (V1), as shown on Figure 2, was closed so that water could not backflow into xylene bottle. The third microorganism injection followed by microbubble injection succeeded in biodegrading the xylene to below

detectable limits. The flow rate in the first two microorganism injections (Runs II-1 and II-2) was 5 ml/min and the microbubbles were injected prior to the bacteria. Before the third microorganism injection (Run II-3), the flow rate was slowed to 3 ml/min, and the microorganisms were injected prior to the microbubbles. While Run II-3 biodegraded xylene successfully, it lasted only 24 hours, so Run II-4 studied the long term effects of biodegradation. A summary of the run specifications in on Table 3.

During Run II-4 and the rest of the experiment, oxygen microbubble injections were performed daily. Microbubbles were injected once the oxygen supply from the previous injection was exhausted. Exhaustion was measured by the effluent xylene concentration or the effluent DO concentration. The criteria for exhaustion was either a xylene concentration above 1 ppm or a DO concentration at 0.1 ppm.

To fulfill the third objective (III), ground water containing 2 ppm ferrous iron and 6 ppm p-xylene was fed to the column for a total flow rate of 3 ml/min during Run III-5. Since the ferrous was being oxidized before it reached the biodegradation zone, the ferrous concentration was increased to 11 ppm (Run III-6).

Table 3

Summary of Run Data

Run#	Avg Inf Xylene Conc. (ppm)	Avg Inf Ferrous Conc (ppm)	Length of run (hr)	CGA injection (ml CGA/ml O2)	# of injections
I-0	8.6	0	230	192/125	2
II-1	6.5	0	24	192/125	1
II-2	6.4	0	24	192/125	1
II-3	7.5	0	24	192/125	1
II-4	7.2	0	348	153/104*	13
III-5	6.8	2.0	295	172/114*	13
III-6	6.1	10.6	405	183/115*	15
IV-7	5.7	9.6	429	159/101*	149

* average for run

To fulfill the fourth objective (IV), an air bubbling section was added prior to the biodegradation zone, as shown in Figure 5. The addition of aerated water was also studied to determine if it was more effective in oxidizing the ferrous.

In fulfilling the fifth objective (V) of flushing the ferric out of the column, the aerated water flow was stopped. A manometer reading was taken prior to stopping feed pumps and closing the valve at the bottom of the column. Approximately four liters of backwashing water was introduced through manometer 3 at rates of 20, 40, 70, 100, 200, 300, 400, and 500 ml/min. The backwashing water exited through a port at the top of the column. Air was also bubbled through to determine its effectiveness in loosening the ferric hydroxide particles. Pressure drops across the column were recorded after each backwashing to determine if any ferric was being removed.

A wash with hydrochloric acid could have been used to solubilize the ferric hydroxide. However, the acid may destroy the microorganisms as it travels downstream from the air sparging zone, so microorganisms may have to be reintroduced to the soil matrix, or the acidic water could be neutralized before it reaches the microorganisms.

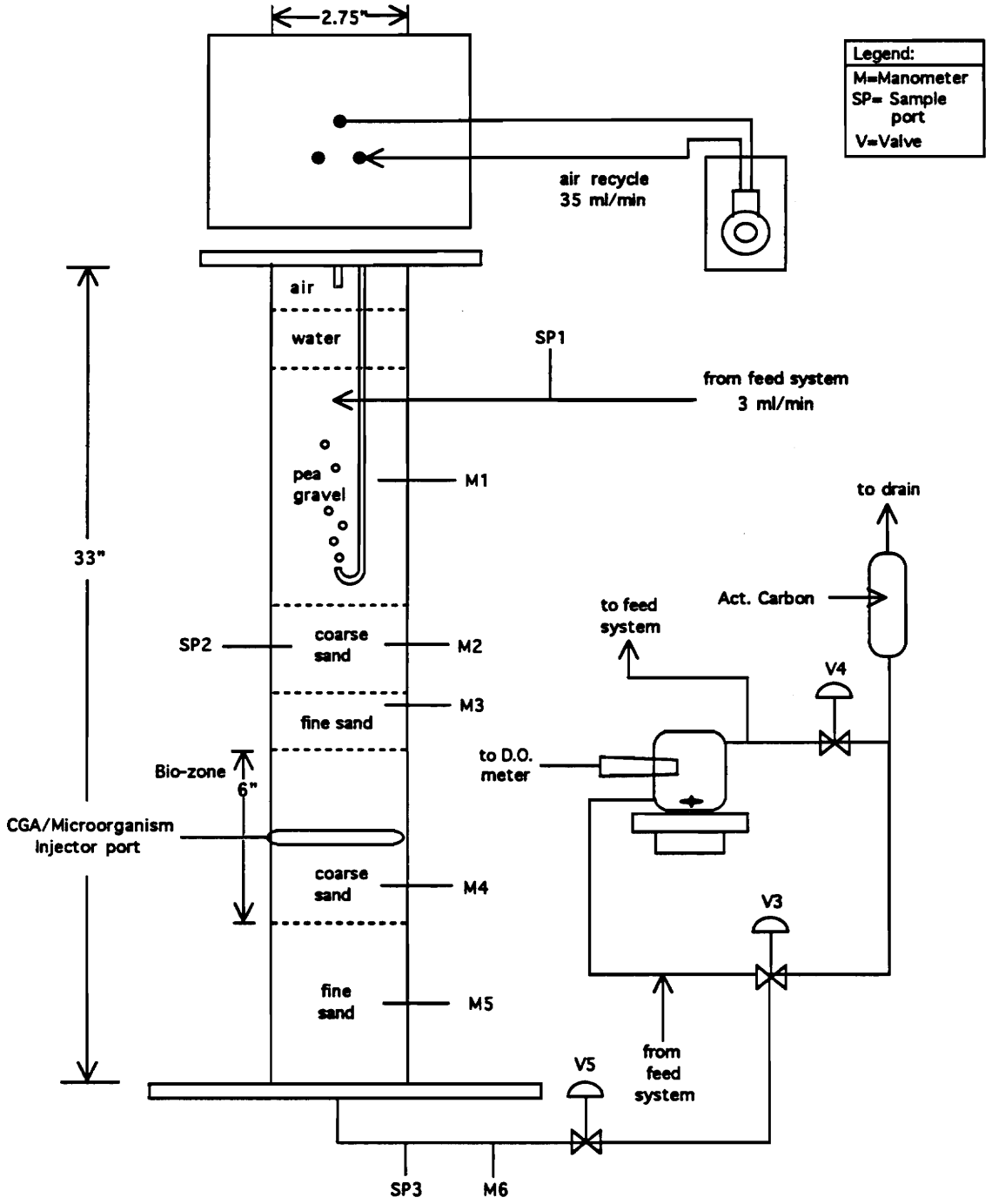

Figure 5: Vertical Column Test Cell with Air Sparging

CHAPTER 4

RESULTS AND DISCUSSION

The first objective was to prove that no xylene was lost to volatilization or adsorption through the system. After a few days the effluent xylene concentration was approximately equal to the influent concentration, and the system was ready for the introduction of microorganisms.

4.1 Biodegradation of p-Xylene

The second objective was to prove that p-xylene can be biodegraded in a soil column and to determine the extent of plugging caused by the microorganisms. The third injection of microorganisms succeeded in biodegrading the xylene. From Figure 6, the xylene concentration dropped to below detectable limits immediately following a CGA injection and remained low until the oxygen supply was depleted.

The groundwater feed, with an average xylene concentration of 7.2 ppm, was pumped to the column at a rate of 3 ml/min. Assuming that every 1 ppm of xylene requires 3.2 ppm oxygen to be oxidized, then 23 ppm of oxygen would be needed to biodegrade the xylene

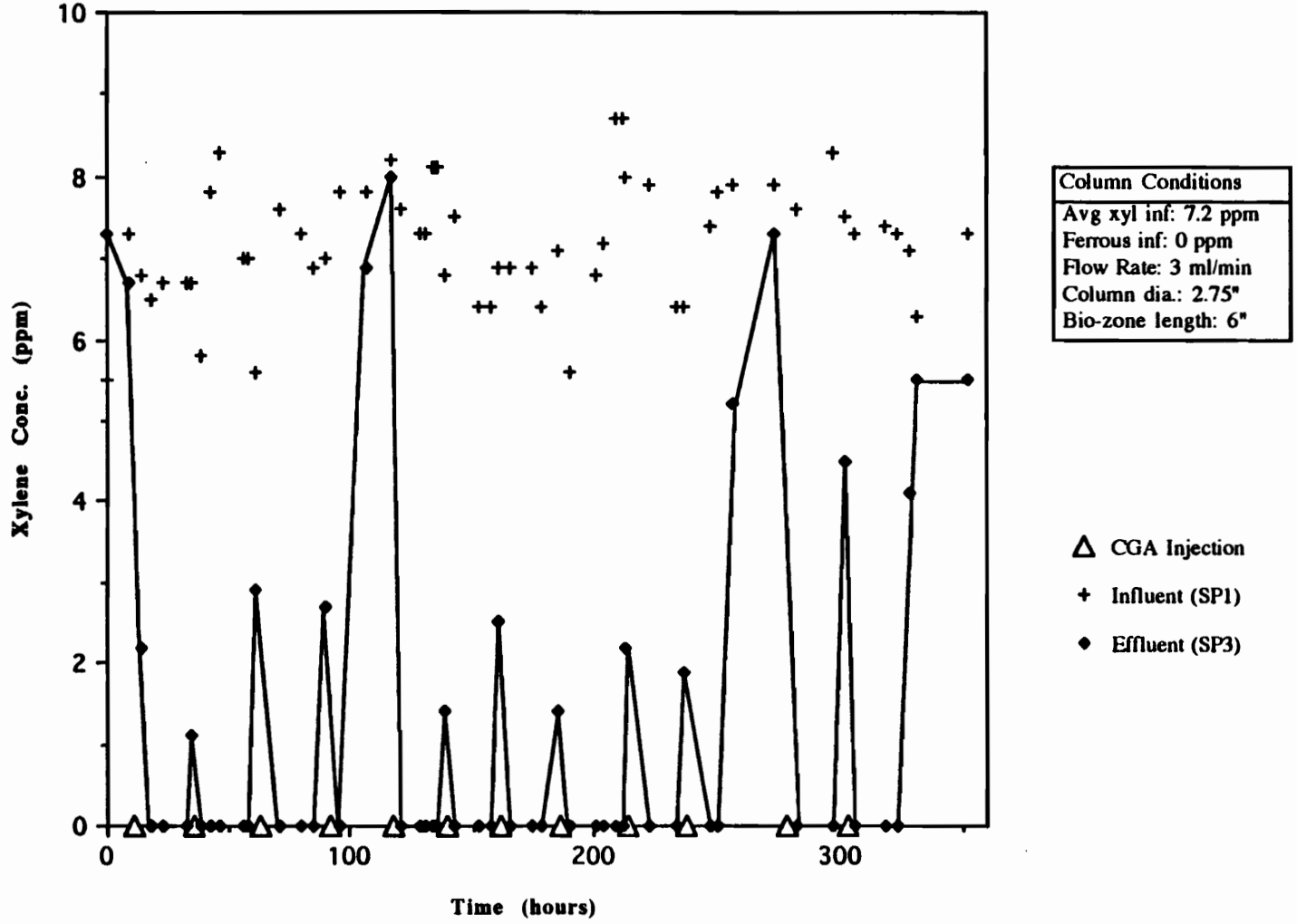

Figure 6: Xylene Concentration as a Function of Time

VCTC - Run II-4

(calculation of oxygen requirement can be found in Appendix B). Before the microorganisms were injected, microbubbles were injected several times and the effluent dissolved oxygen monitored. During these injections, the effluent DO peaked at over 20 mg/l. A few hours prior and a few hours after the peak the DO was between 10 and 13 mg/l. A dissolved oxygen level of 12 ppm would only oxidize 4 ppm xylene, while results from this test indicate that the microorganisms were degrading 7 ppm xylene for approximately 24 hours. If some of the xylene is contributing to formation of new cell matter, then the microorganisms would not need as much oxygen than was calculated, unless the system has reached steady state.

Figure 7 defines how the oxygen was utilized in Run II-4. The material balance was around the whole column - influent sample port (SP1) to effluent sample port (SP3). The difference in the influent DO and effluent DO was the amount of oxygen dissolved into the flowing ground water. The difference in the influent and effluent xylene concentrations was assumed to have been biodegraded. For every ppm of xylene degraded, 3.2 ppm of oxygen were oxidized. Overall 69.9% of the injected oxygen contributed to xylene biodegradation. An overall efficiency of 89.0% was determined, assuming the surfactant was biodegraded. Vent losses, from the top of the column, in this part of

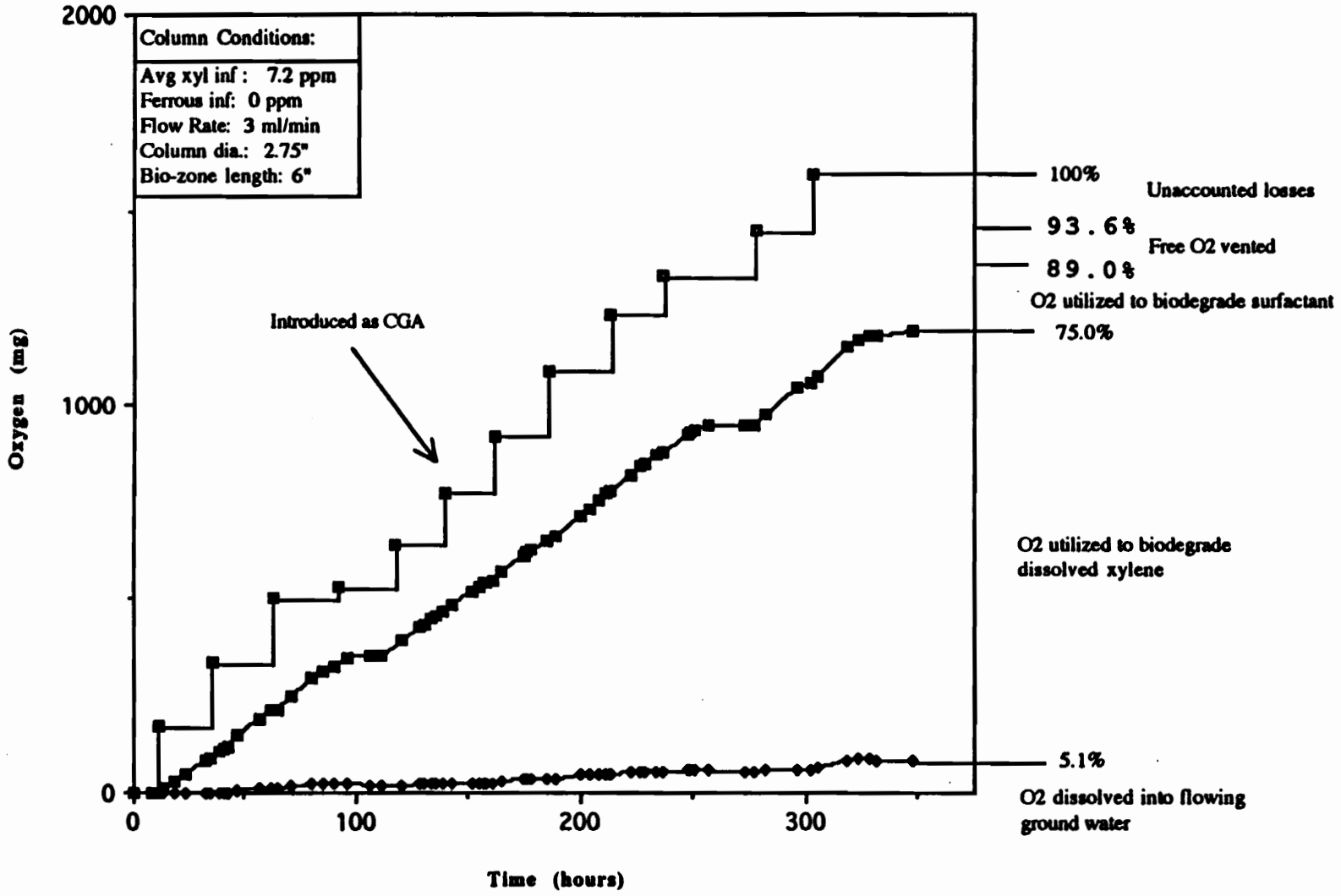

Figure 7: Oxygen Material Balance

VCTC - Run II-4

the experiment were only 4.6% of the injected oxygen, as the microbubbles had not channelled through the fine sand layer yet.

The pressure drops over the biodegradation zone, as shown in Figure 3 (M3-M5), are plotted in Figure 8. The reported readings were taken prior to a CGA injection when the microbubbles had been depleted. This way the increase in pressure caused by the microbubbles is negated, and the reported pressure drop represents the amount caused by biodegradation. Figure 8 shows an increase in pressure until the sixth day. The pressure drop held relatively constant for about four days and then started declining.

This result shows promise for *in situ* biodegradation since previous research on glucose biodegradation resulted in high pressure drops. If the biodegradation process were to cause plugging, then *in situ* degradation would not be feasible as groundwater flow through the biodegradation area would be limited and would prevent the contamination from reaching the microorganisms.

The oxygen mass transfer coefficients for this test ranged from 0.01 to 0.43 hr^{-1} with an average value of 0.24 hr^{-1}. The coefficient was highest immediately after a CGA injection and then decreased until microbubbles were reinjected. Even when the mass transfer coefficient was

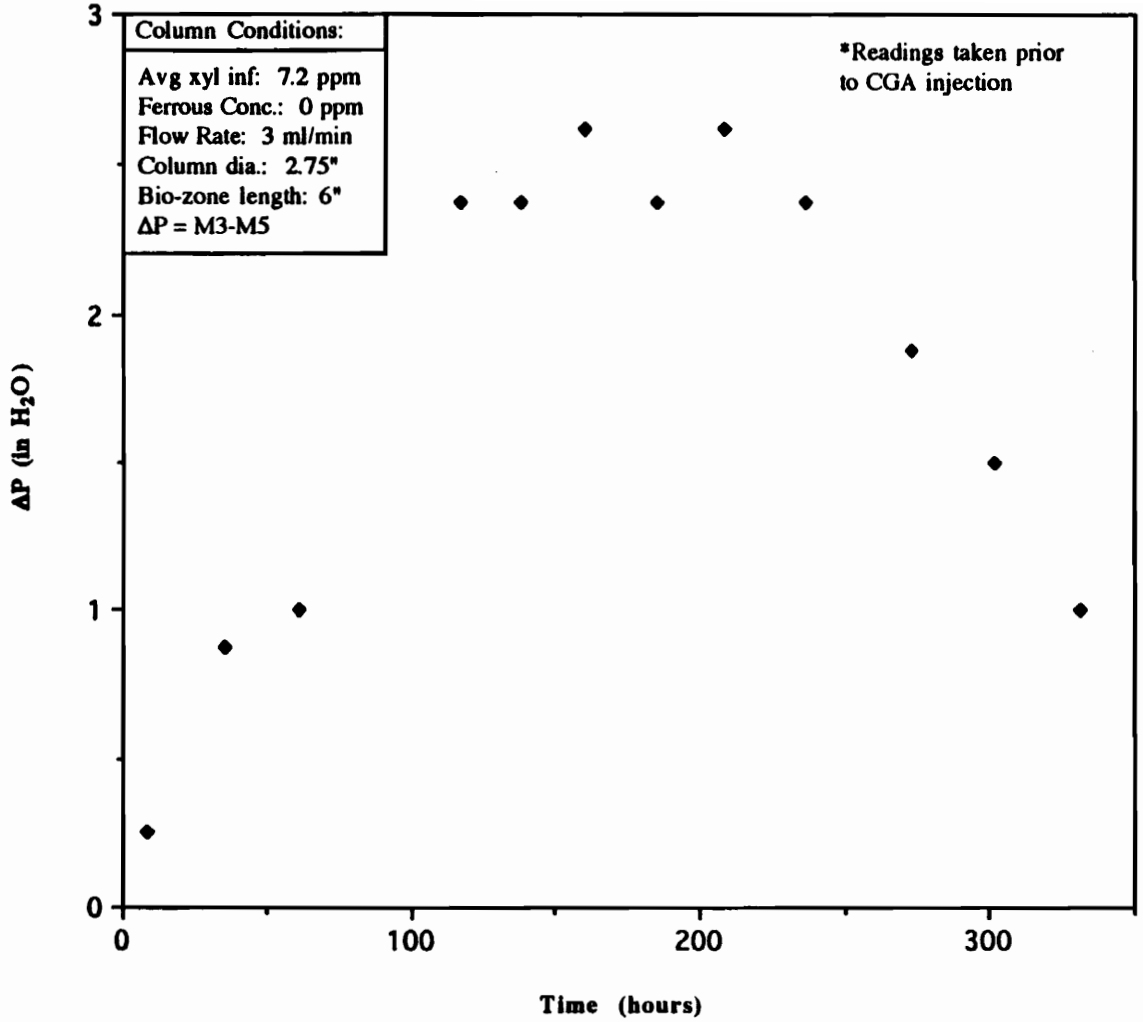

Figure 8: Pressure Drop Over Bio-zone as a Function of Time

VCTC - Run II-4

low, the microorganisms still biodegraded the xylene until the oxygen supply was completely exhausted. It is also possible that the xylene was adsorbed onto the surface of the biofilm, until oxygen was reinjected, and the microorganisms could biodegrade the xylene. In future testing, total organic and inorganic carbon levels should be measured in order to determine if the xylene is being completely biodegraded to carbon dioxide and water.

These coefficients correspond to values obtained in previous work using a 3.75 inch diameter column which ranged from 0.07 to 0.40 hr^{-1} (Michelsen et al 1991). Values for the VSTC were considerably lower ranging from 0.01 to 0.09 hr^{-1} which could indicate that, in the field, oxygen transfer might not be as good as in column testing.

So, in vertical slice test cell testing and in field testing, oxygen microbubbles may need to be injected more frequently. In this research, the hold-up time was approximately 45 minutes. However, the contaminated ground water will have a longer residence time in the biodegradation zone in the VSTC (as much as 24 hours or more), so the microorganisms may be able to degrade a similar or greater concentration of xylene.

4.2 Xylene Biodegradation and Ferrous Oxidation

To fulfill the third objective, initially a 2 ppm ferrous and 6 ppm xylene stream was fed to the column (Run III-5). The ferrous was being oxidized before it reached the biodegradation zone due to breakthrough of the microbubbles. There was also no appreciable increase in head loss. Therefore, the ferrous concentration was increased to 10 ppm, and the xylene concentration remained constant (Run III-6).

After increasing the ferrous concentration, the ferric hydroxide precipitate was observed in the column only in the area that the microbubbles occupied. Since the ferrous was oxidizing where the microbubbles were located, the ferric iron could be used as an indicator of oxygen transfer to ground water. Since the microorganisms also need oxygen, one could assume that they are living in the zone where the ferric hydroxide is, since this is where most oxygen is being transferred.

The xylene and ferrous concentrations are plotted against time on Figure 9. A portion of the run is plotted here to illustrate the concentration profile. When the oxygen has been depleted, the xylene concentration appears to increase after the ferrous concentration starts increasing. The rest of the experimental run (hours 100-

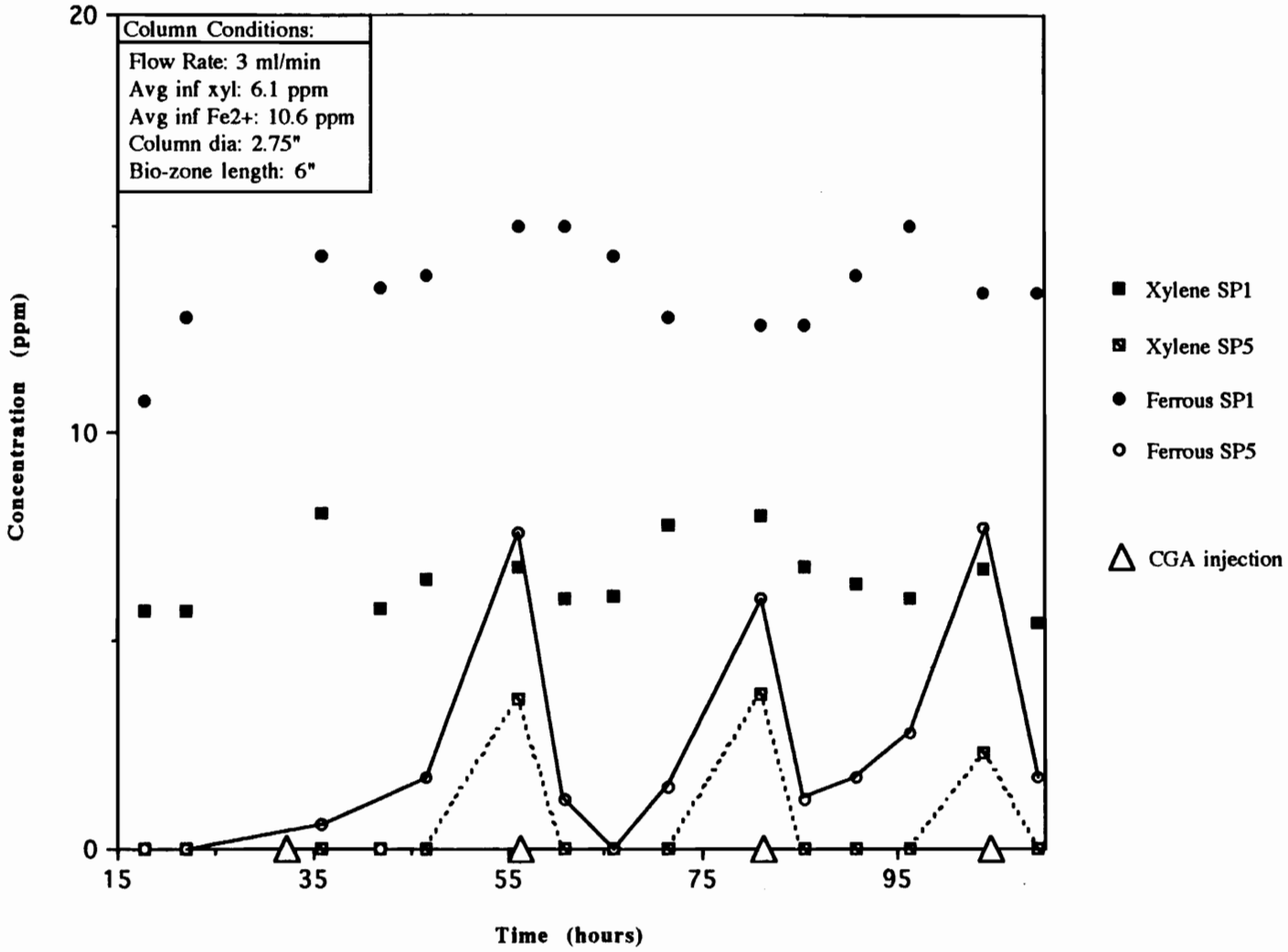

Figure 9: Xylene and Ferrous Iron Concentrations

VCTC - Run III-6

400) shows the same trend and the figures can be found in Appendix C. These results indicate that the high concentration of iron does not inhibit the xylene biodegradation as previously thought from glucose biodegradation testing.

The oxygen material balance is illustrated on Figure 10. The ferrous oxidation was calculated by assuming that the oxidation of 7 ppm ferrous requires 1 ppm oxygen . In this test, more microbubbles were breaking through the fine sand layer above the biodegradation zone and rising to the top of the column. This volume of oxygen was collected as soon as possible and recorded as vent losses which consisted of 150 ml of the 1725 ml of oxygen injected as oxygen microbubbles. In this run, only 13.3% of the oxygen was unaccounted.

The pressure drops, reported in Figure 11, were again the value prior to a CGA injection. The head losses reveal no trend for this run, which is a positive result, since dramatic increases in pressure were expected for a high concentration of ferrous in the feed.

The mass transfer coefficients for this test ranged from 0.12 to 0.49 hr^{-1} with an average of 0.29 hr^{-1}. These values are similar to those calculated for Run II-4.

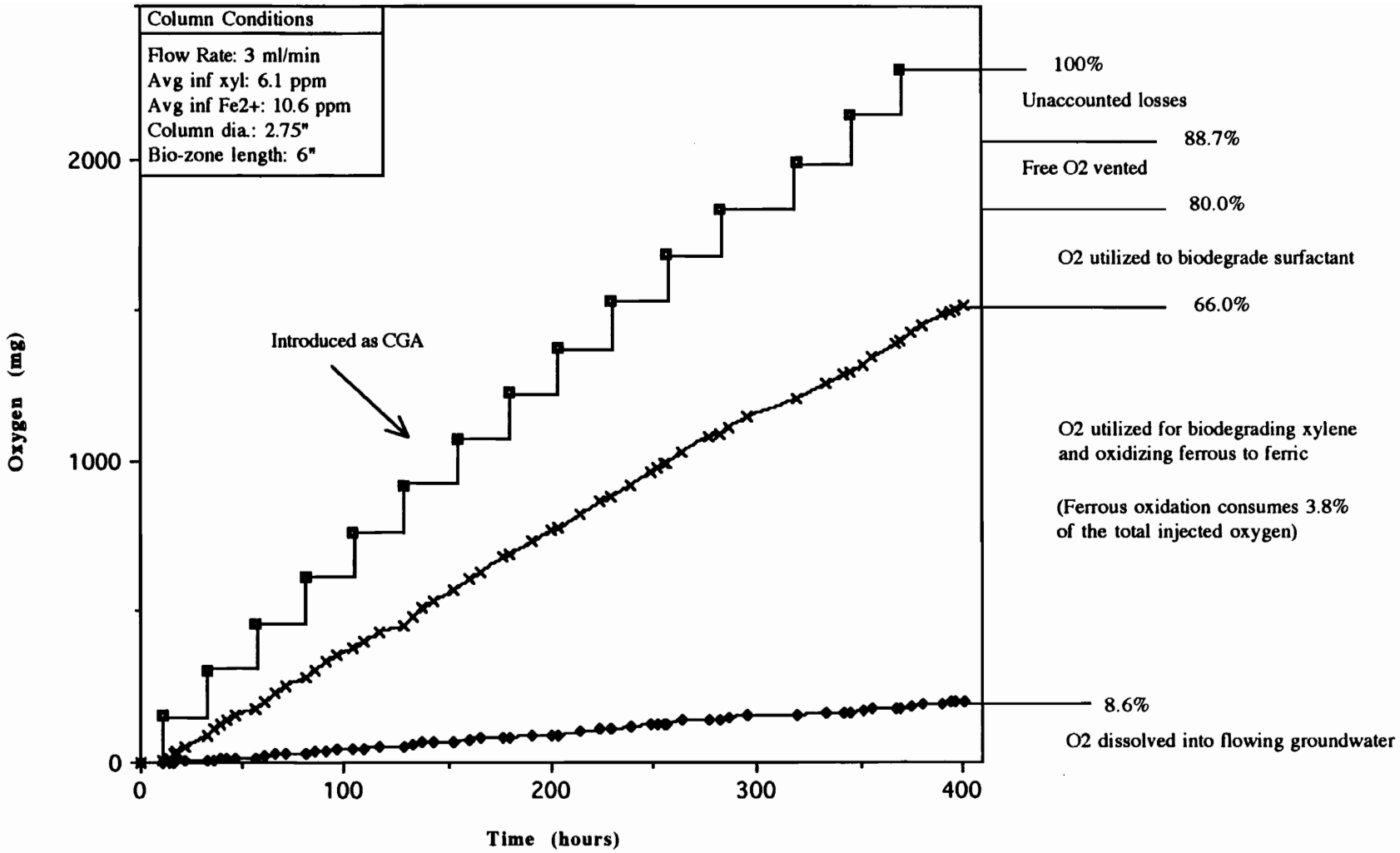

Figure 10: Oxygen Material Balance

VCTC - Run III-6

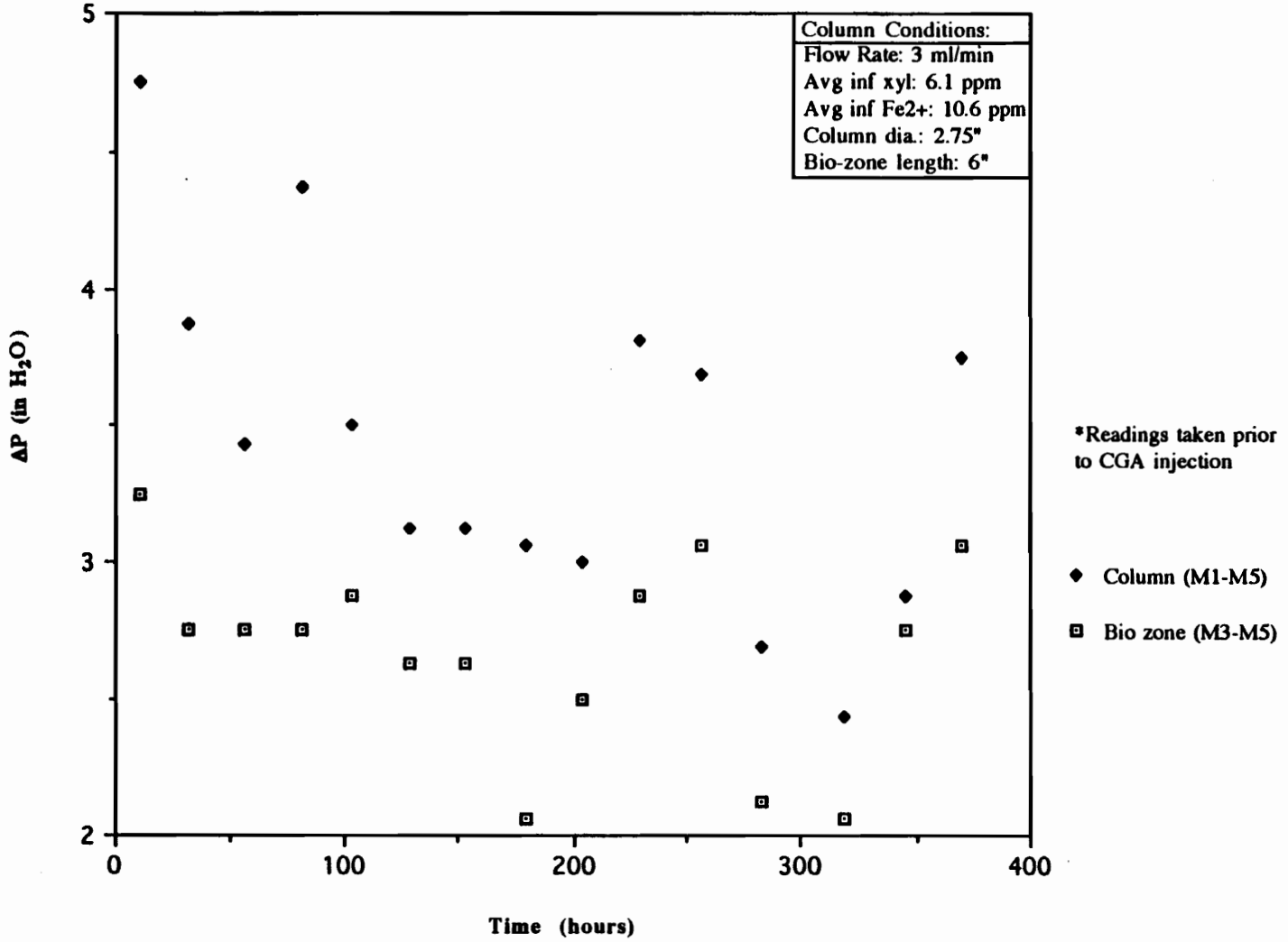

Figure 11: Pressure Drop as a Function of Time

VCTC - Run III-6

4.3 Air Sparging and Biodegradation

The fourth objective in the research was to oxidize the ferrous before it entered the biodegradation zone and to attempt to remove the ferric precipitate from the sand matrix. An air sparging zone was added to the top part of the column. The air was continuously recycled and replaced approximately every day.

In this test, only 59.0% of the oxygen is accounted for, as shown in Figure 12. Vent losses could not be determined since there was head space at the top of the column due to the air sparging recycle system.

The oxygen mass transfer coefficients for this run ranged from 0.006 to 0.30 hr^{-1} with an average of 0.17 hr^{-1}. These coefficients are lower than the values calculated in runs II-4 and III-6.

The main difference in this run was that the microorganisms were degrading an average of 3.4 ppm xylene, whereas in runs II-4 and III-6 the microorganisms were degrading 6 to 7 ppm. Part of the lower oxygen transfer could be due to error in the DO meter, if at high dissolved oxygen concentrations the meter gives a reading 0.5 mg/l lower than actual as suggested by the Winkler method. An increase of 0.5 mg/l for each DO reading in this run would

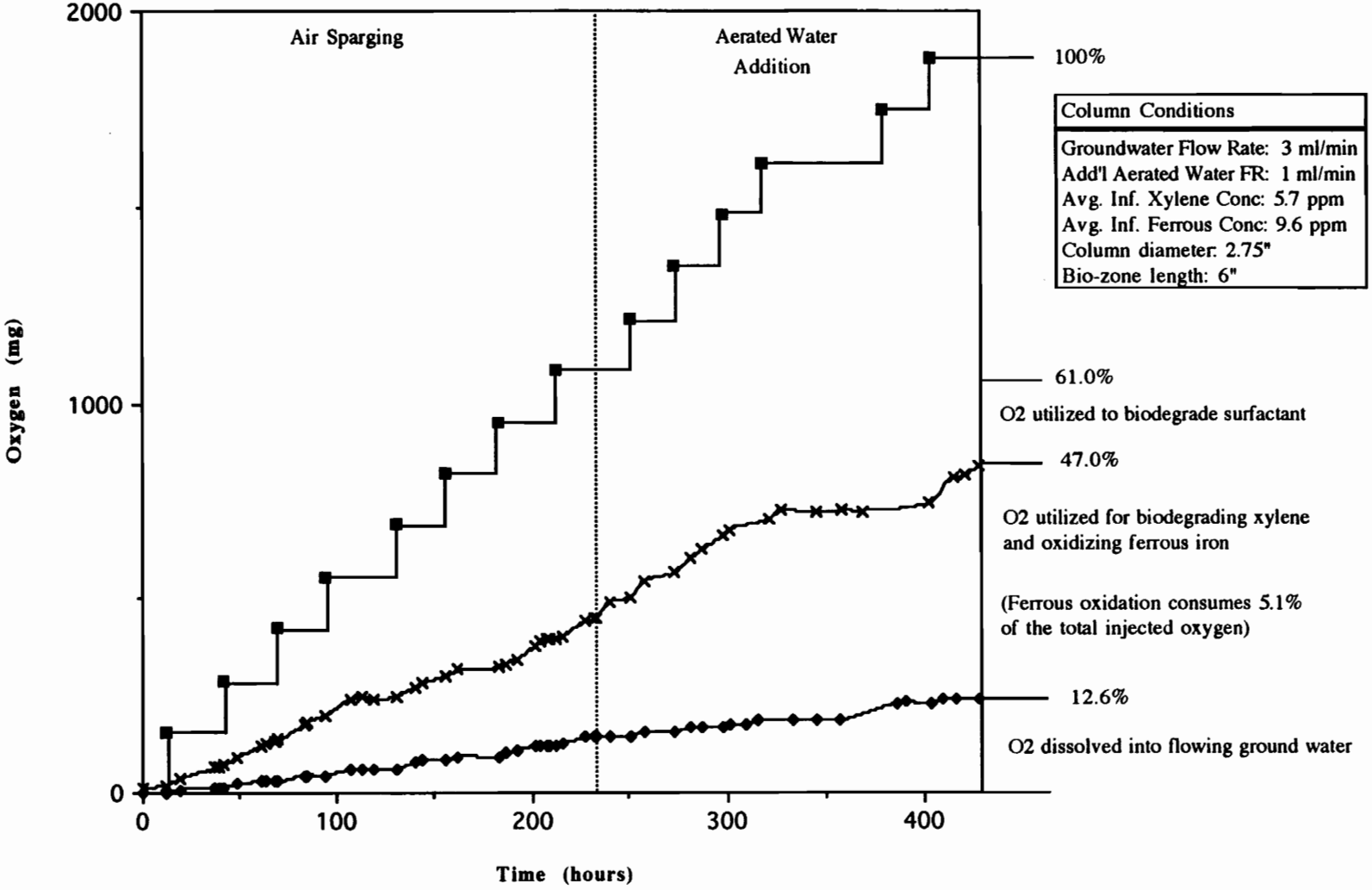

Figure 12: Oxygen Material Balance

VCTC - Run IV-7

result in an increase of 3% in the overall oxygen utilization.

The head losses over the biodegradation zone (M3-M5) and over the column (M1-M5) for this run are shown in Figure 13. Manometer positions are illustrated on Figure 5. As in the last test, the pressure drops show no trend, which would indicate that the ferric precipitate is not causing a steady increase in pressure drop as in previous research. The trend, shown in Figure 13, may have resulted from ferric precipitate particles partially plugging the soil matrix, and then later becoming dislodged in such a way as to reduce the ΔP.

From Figure 14, the air sparging zone was stripping as much as 4 ppm of xylene out of the influent stream which had an average concentration of 5.7 ppm. Figure 15 indicates that the air sparging zone was oxidizing at most 3 ppm ferrous iron for part of the run and was not oxidizing any ferrous for most of the run. The average influent ferrous concentration was 9.9 ppm, and the average pre-biozone ferrous concentration was 8.9 ppm. So, an average of 1 ppm ferrous was being oxidized. These results indicate that the air sparging zone was succeeding in stripping the xylene and not oxidizing the ferrous iron.

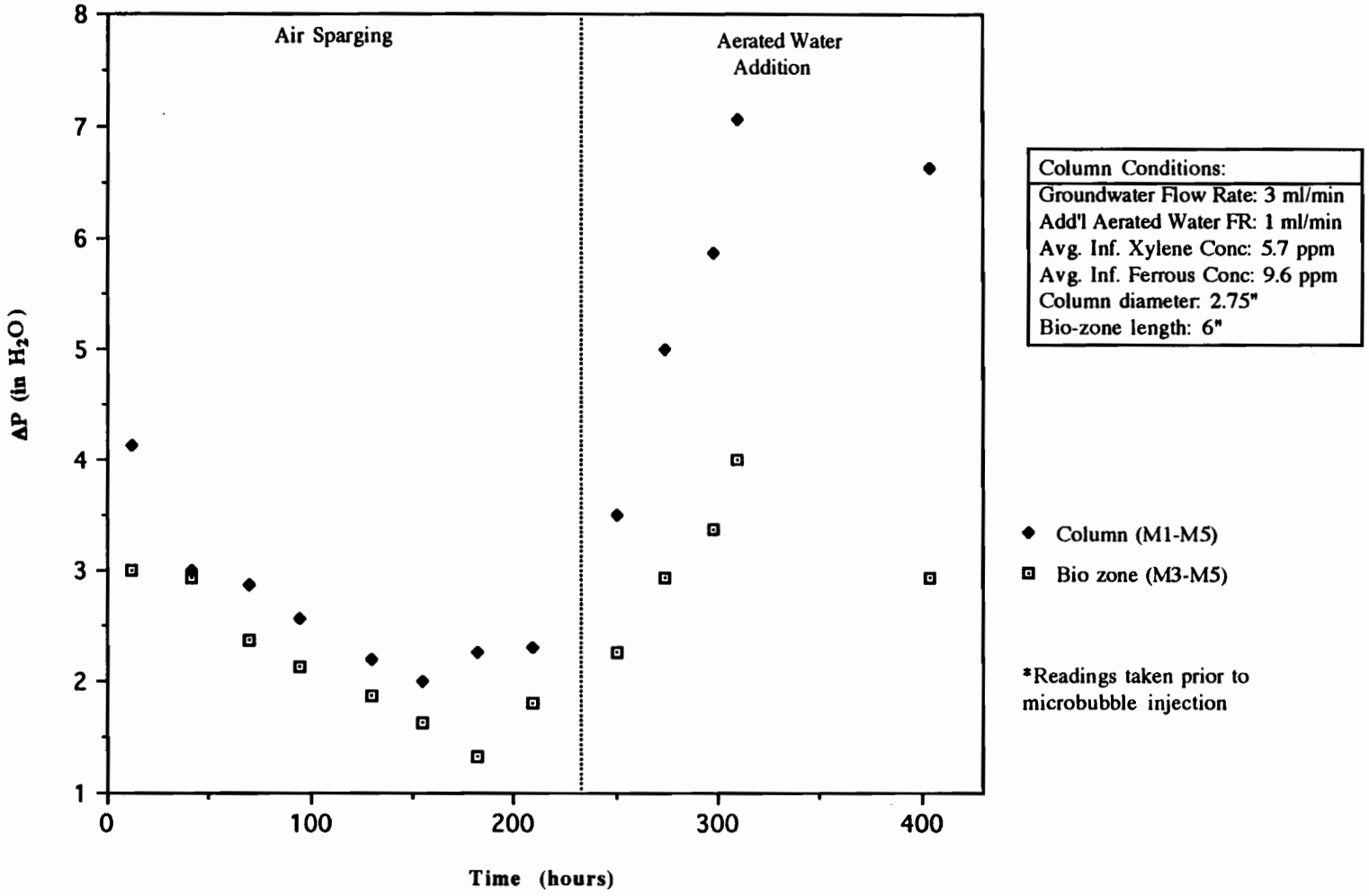

Figure 13: Pressure Drop as a Function of Time
VCTC - Run IV-7

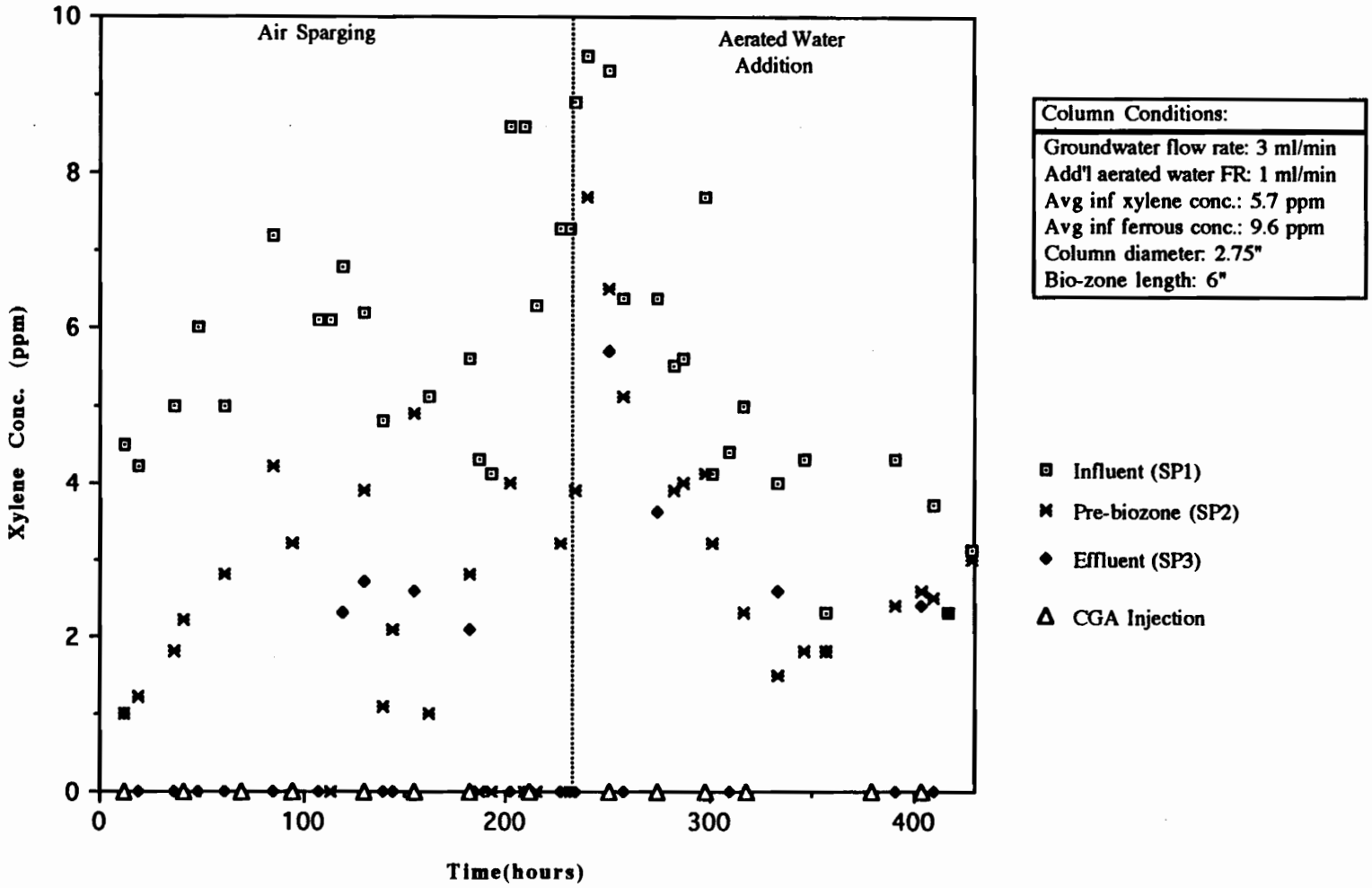

Figure 14: Xylene Concentrations as a Function of Time
VCTC - Run IV-7

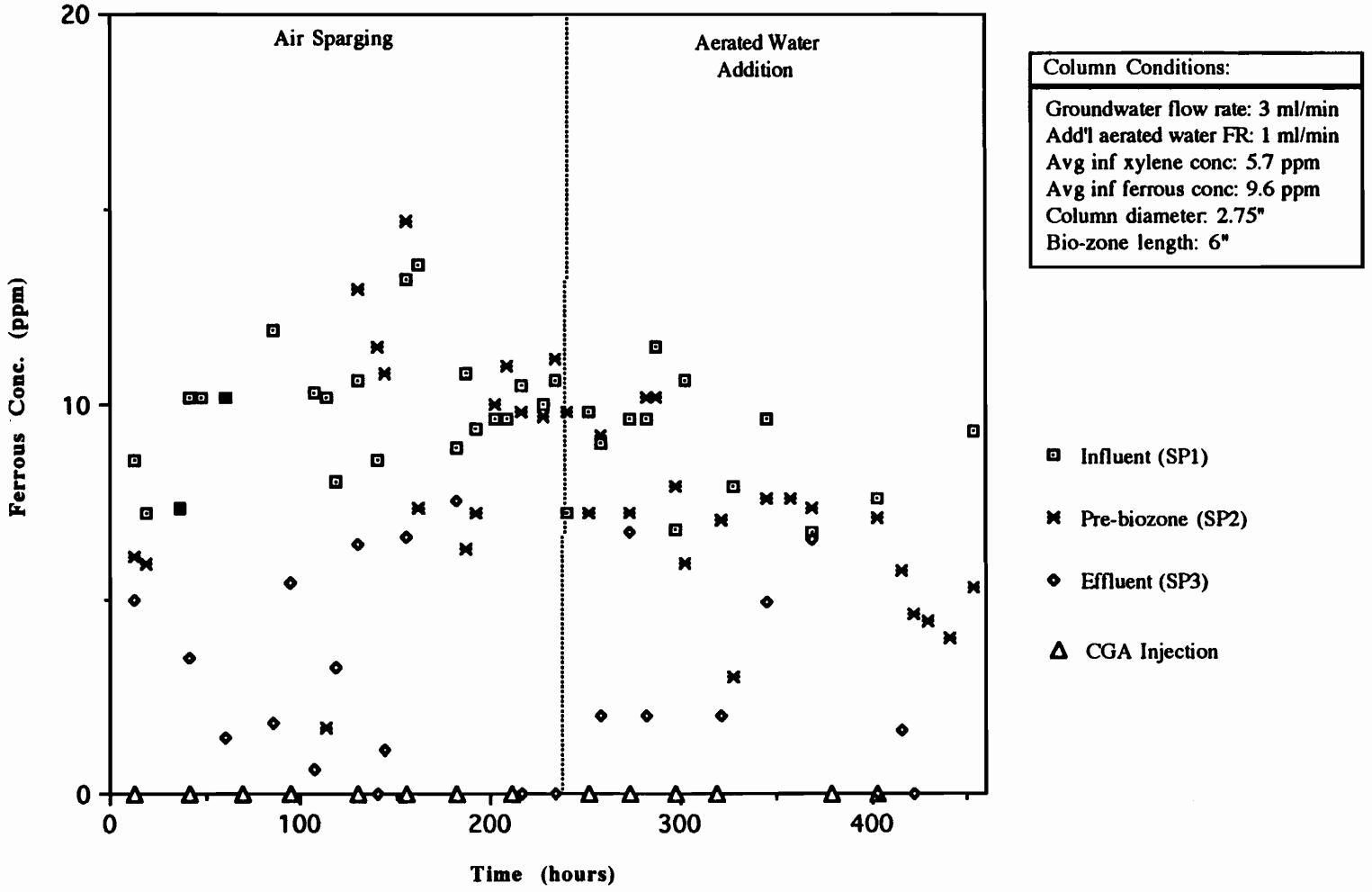

Figure 15: Ferrous Concentrations as a Function of Time

VCTC - Run IV-7

The rate of ferrous oxidation is dependant on pH. An increase of one pH unit can raise the reaction rate a hundred times. Stumm and Lee (1961) have determined the reaction time for ferrous oxidation as a function of pH and ferrous concentration. Depending on the concentration, the reaction could take an hour at a pH of 7. In this experimental work, the ferrous iron may not have had an hour of contact time in the air sparging zone since the residence time was approximately two hours.

Therefore, better air delivery system would be desirable in future testing, such as some type of sparger. Smaller bubbles have a lower rise velocity, which would increase the contact time between the air bubbles and ground water. This should increase the amount of oxygen transferred and therefore the amount of ferrous oxidized should increase. However, the increased contact time will also increase the amount of xylene volatilized which is not desirable.

Next, aerated water was fed to the column at a rate of 1 ml/min to determine if it could oxidize the ferrous iron better than the air sparging. The aerated water was introduced at the top of the column in a separate port from the ground water feed. For this part of the run, the average influent ferrous concentration was 8.9 ppm, and the average pre-biozone ferrous concentration was 7.1 ppm.

Accounting for the dilution of 3 ml/min to 4 ml/min, the aerated water was no more effective in oxidizing the ferrous than the air sparging. The pH during the run was raised from 6 to 7 to determine if more ferrous would be oxidized due to a higher ^{-}OH concentration, but no change in the effluent ferrous concentration resulted.

Towards the end of the run, at 428 hours, the aerated water feed port was moved to the same port where the ground water feed enters. From Figure 15, these last pre-biozone ferrous concentrations are slightly less than the previous values which would indicate that good mixing would be required, if ferrous oxidation using aerated water was desired.

4.4 Ferric Iron Removal

To fulfill objective five, the air sparging zone was flushed with water or air and water to remove the ferric precipitate and reduce the pressure drop. Backwashing water was introduced through manometer 3 and exited at the top of the column. The results of the ferric iron removal test are summarized in Table 4. During tests where air was added prior to water, cloudiness was noted at the top of the column where the ferric precipitate had been dislodged.

Table 4

Ferric Iron Removal

Water Flow Rate (ml/min)	Amount (l)	Amount of Air Added (l)	ΔP (in)
20	0.9	0	3.3750
40	2.0	0	2.7500
40	4.5	0	3.4400
70	4.5	0	2.7500
100	4.5	200	2.0000
100	4.25	250	2.8750
200	4.0	250	1.8750
300	4.5	0	1.7500
400	4.0	0	1.8125
500	4.0	0	1.1250

In tests where no air was added, this cloudiness was not noted. After the first four water flushes, the pressure drop between manometers 1 and 5 had decreased by 0.625". Then, three air and water additions resulted in pressure drop decreases of 0.875". The last three water additions at high flow rates decreased the pressure drop by 0.75". The results of this test indicate that high flow rate, around 500 ml/min for 38.3 cm^2 of area, and a large volume of water (4 l) or alternating air and water flow would be needed to reduce the pressure drop. If the treatment trench consisted of sand matrix only, then either iron removal method would be applicable. If the treatment trench had alternate clay and coarse sand layering then the air addition would not be practical as it could cause breakthroughs in the clay layer.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

This research studied *in situ* biodegradation of xylene in a soil column using oxygen microbubbles to supply the electron acceptor. The results show promise for *in situ* biodegradation and could lead to pilot scale testing and eventually field testing.

The first objective of proving no xylene was lost to adsorption or volatilization was achieved through the system design and by allowing the experiment to reach steady state with respect to xylene concentration before introducing the microorganisms.

To fulfill the second objective, xylene degrading microorganisms were introduced into the column. The bacteria degraded xylene to below detectable limits until the oxygen supply was exhausted. Oxygen microbubbles were reinjected daily once the oxygen supply was depleted for about two weeks. The pressure drops over this time showed a slight increase over the first few days and then a gradual decline, which shows promise for *in situ* biodegradation as the microorganisms were thought to cause plugging. An overall oxygen utilization of 86.2% was obtained for the xylene

biodegradation test. The oxygen utilization was much better than previous testing using microbubbles.

The third objective was to study biodegradation in the presence of ferrous iron and to monitor the pressure drops as the ferric precipitates can also cause plugging. This run showed no interference from the ferrous iron. The microorganisms seemed to get the oxygen that they needed before the ferrous could oxidize. The pressure drops showed no general trend, therefore the ferric precipitate did not cause an appreciable amount of plugging. An overall oxygen utilization for this run was 77.1% with 85.8% of the oxygen accounted for including 8.7% free oxygen vented.

Results from the previous test indicate that the ferrous does not interfere with the biodegradation test and that it does not plug the soil matrix. However, after an extended period of time, the ferric hydroxide may plug the soil matrix. Therefore, the fourth objective studied the effectiveness of an air sparging zone in removing the ferric precipitate prior to the biodegradation zone.

The air sparging zone resulted in volatilization of the xylene and very little ferrous precipitation. Elevation of the pH from 6 to 7 resulted in no increase in ferric precipitation in the air sparging zone. Aerated water resulted in very little ferrous precipitating either.

However, oxygen microbubbles proved to precipitate the ferrous iron better than air sparging or aerated water addition regardless of the pH without volatilizing xylene. The major disadvantage of using oxygen microbubbles rather than air sparging is the elevated cost.

The oxygen utilization for this run was 58% which is considerably lower than the previous two tests. Since one major difference in this part of the experiment is that the bacteria were not degrading as much xylene, the microorganisms seem to be facilitating the oxygen mass transfer. Possibly, the microbes do not need as much oxygen as originally thought, since some of the xylene may be contributing to new cell formation.

The fifth objective was to attempt to flush the ferric precipitate from the column. Results from this test indicate that either a backwash flow close to the fluidization velocity (500 ml/min for 38.3 cm^2) or alternate air sparging and backwashing is needed to remove the ferric precipitate. Future testing should attempt removal of the ferric hydroxide by lowering the pH.

One recommendation that arose from this research is to monitor the total organic and inorganic carbon entering and leaving the column to determine if the xylene is being completely oxidized to carbon dioxide and water. This would

be most suited to column testing since better closure can be obtained.

Also, the simultaneous biodegradation of a mixture of contaminants, such as benzene, toluene, ethylbenzene, para-, meta-, and ortho-xylene, should be studied in a column or in the vertical slice test cell. Use of the vertical slice test cell is recommended for future testing since column testing may be somewhat idealized.

Oxygen transfer may not be as good in the VSTC, as indicated by lower mass transfer coefficients, since there is room for the ground water to channel around the CGA cloud. In column testing, the CGA cloud occupies the whole cross-sectional area, so the ground water is forced through the CGA cloud. Therefore, in vertical slice cell testing, CGA injections may need to be performed more often. However, the biodegradation zone is longer (approximately 3 feet in length), so an increased residence time will provide more time for oxygen transfer and for biodegradation. Complete biodegradation of a similar or higher concentration of contaminant may be obtainable in the VSTC, but it must be tested.

Studying the precipitation of ferric iron for an extended period of time is also recommended, as the ferric precipitation is eventually expected to cause plugging. A pre-precipitation zone consisting of pea gravel could remove

the ferrous iron before the ground water reaches the biodegradation zone. For testing in the VSTC, a separate air sparging cell could be added prior to the VSTC. This cell would contain pea gravel with an air delivery system positioned at the bottom of the cell. A better delivery system should be used in future testing to increase the transfer of oxygen to ground water. Then, removal of the ferric precipitate by several ways should be attempted. A combination of air sparging and backwashing could be used. Also, an acid wash should be attempted to determine its feasibility. The acid may destroy the microorganisms, so either the acid would have to be neutralized, or microorganisms would need to be reintroduced into the subsurface.

A remediation plan for *in situ* biodegradation will depend on the site characteristics. For field testing, any free product remaining in the subsurface should be recovered by pumping. Injection wells could be placed in the area that contains the largest amount of contaminated ground water. Through these wells, microorganisms, microbubbles, and nutrients could be introduced to biodegrade the contaminants. If the contaminated ground water is also flowing, then a treatment trench could be placed downstream to remove the remaining contamination from the ground water.

Results from this research indicate that field testing *in situ* biodegradation should be attempted in the near future. The microorganisms did not cause an appreciable amount of plugging in this research. The oxidation of ferrous iron did not interfere with the biodegradation process, and the ferric hydroxide precipitate did not cause an appreciable amount of plugging. Microbubbles have proven to be the optimum mode of oxygen transfer. They precipitate the ferrous iron regardless of pH while still supplying the microorganisms with oxygen.

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Appendix A:

Data Tables

Table A1: Data for Runs I-0 through II-3

Run #	Time (hours)	Flow Rate (ml/min)	Inf. DO (ppm)	Eff DO (ppm)	Inf Xyl (ppm)	Eff Xyl (ppm)	Kla (hr^{-1})	mg O2 trans	mg O2 cum
I-0	0	5.3	0.6	0.8	8.7	9.0	0.0043		
	12.75	5.0	1.2	0.8	9.4	7.7	-0.0083		
	17.50	4.7	1.7	1.1	12.3	8.3	-0.0118		
	22.92	4.5	1.2	1.2	11.9	11.8	0.0000		
	27.75	4.0	0.4	0.4	10.6	5.3	0.0000		
	36.75	3.5	1.3	0.9	10.7	10.3	-0.0058		
	41.33	5.0	1.3	1.2	8.0	13.0	-0.0021		
	46.75	5.0	0.5	0.8	7.8	7.5	0.0061		
	52.08	5.0	1.0	1.0	5.6	9.4	0.0000		
	60.75	5.0	1.1	0.8	8.9	9.2	-0.0041		
**	63.25							0.00	0.00
	66.25	5.0	0.9	14.3	9.7	8.0	0.3422	12.06	12.06
	70.92	5.0	0.3	20.0+ *	7.2	7.9	0.5637	27.60	39.66
	75.92	5.0	0.3	10.7	11.4	7.8	0.2466	15.60	55.26
	84.75	5.0	0.9	1.8	5.0	9.4	0.0188	2.38	57.64
	89.75	5.0	0.9	0.4	9.3	7.6	-0.0102	-0.75	56.89
	94.75	5.0	1.0	0.3	7.3	7.9	-0.0143	-1.05	55.84
	99.17	5.5	0.8	0.9	8.2	8.2	0.0023	0.15	55.99
	108.75	5.0	0.9		8.0	8.8	0.0000	0.00	55.99
**	112.50							0.00	0.00
	113.75	5.0		7.4	8.6	4.6	0.1472	2.44	2.44
	115.00			13.5			0.3169	4.73	7.16
	116.17			16.2			0.4058	5.37	12.53
	117.17	5.0		20.0+			0.5514	5.73	18.26
	120.75	5.0		10.6			0.2316	10.42	28.68
	122.92	5.0		8.8	8.7	6.3	0.1830	5.14	33.82
	133.83	5.0	1.1	2.0	8.9	5.8	0.0189	2.95	36.77
	157.75	5.0	1.0	0.4			-0.0123		
	162.75	5.0		0.2	6.5	8.8	-0.0164		
	183.75	5.5	0.9	0.8			-0.0023		
	191.42	5.0	0.5	0.2	9.3	8.9	-0.0061		
	195.92	5.0	0.6	0.1	7.8	7.1	-0.0102		
	205.92	4.5	0.5	0.2	9.2	9.4	-0.0055		
	215.75	5.0	0.6	0.2	7.6	7.6	-0.0081		
	220.42	5.0	0.8	0.2	8.7	8.0	-0.0122		
	228.83	5.0	0.5	0.2			-0.0061		
	230				5.7	6.3			
II-1	231.42	#							
	232.25	5.0		0.1	6.0	5.9			
	233.25			1.7					
	234.25			2.2	6.7	5.1			

* DO reading off scale
** CGA injection of 192 ml CGA at this time
# 199 ml CGA injected, followed by microorganism injection

Table A1 (con'd): Data for Runs I-0 through II-3

Run #	Time (hours)	Flow Rate (ml/ min)	Inf. DO (ppm)	Eff DO (ppm)	Inf Xyl (ppm)	Eff Xyl (ppm)	Comments
	235.75			3.0	6.5	5.4	
	236.58	4.9		10.0			
	237.75			8.3			
	240.25	5.0		4.4	7.6	0.7	
	244.08		0.9	0.1	8.0	2.3	
	255.25	5.0		0.1	5.3	5.7	
	260.75			0.2	7.0	6.5	
	269.5	5.0		0.2	6.7	4.4	
	272.25	5.0		0.1	7.7	8.5	
	279.33	5.0	1.0	0.1	5.0	7.2	
	291.25	5.0			7.0	6.2	
II-2	293.25						CGA injection, 192 ml CGA, followed by microorganism injection
	294.92			4.5	6.1	3.7	
	298.08	5.0		5.4	7.7	4.8	
	301.25	4.9	1.3	1.7	6.6	3.2	
	313.25	4.8	0.7	0.3	6.4	6.4	
	324.75	3.1		0.4	6.8	6.9	
	326.75	3.2	0.5	0.2	6.4	8.0	
	332.25	3.2	0.5	0.4	6.5	6.2	
II-3	333.25						Microorganism injection, followed by CGA injection, 192 ml CGA
	335.00			1.2	5.4	1.5	
	337.00			6.9	7.1	6.7	
	338.00	3.0		5.3		5.3	
	339.00	3.0		6.1	7.9	0.0	
	341.33	3.0		6.4	7.3	0.0	
	342.25	3.0		7.3		0.0	
	343.58	3.0		4.2	8.0	0.0	
	346.42	3.1		2.0	7.8	0.0	
	347.25			5.2			
	350.42	3.1		6.0		0.0	
	357.75	3.2		0.9	7.1	0.0	
	358.75			0.6			
	359.75			0.1			
	361.00	2.9		0.1	7.2	4.5	
	361.75		0.6	0.1		5.1	
	362.50			0.1		5.5	
	363.50			0.1		5.7	
	364.25	3.1		0.1			

Table A2: Run# II-4 Data

Time (hours)	Inf. DO (mg/l)	Eff DO (mg/l)	Flow Rate ml/min	Oxygen trans (mg)	Cum O2 trans (mg)	Inf Xyl Conc (mg/l)	Eff Xyl Conc (mg/l)
0.00	1.00	0.40	3.00	0.00	0.00	5.50	7.3
8.50	0.90	0.10	3.00	-1.22	-1.22	7.30	6.7
10.75	0.90	0.10	3.00	-0.32	-1.55		
13.50	0.90	1.90	3.00	0.50	-1.05	6.80	2.2
18.25	0.90	2.60	3.00	1.45	0.40	6.5	0
22.75	0.90	1.80	3.00	0.73	1.13	6.7	0
32.50	0.90	0.30	2.90	-1.02	0.11		0
34.75	0.90	0.10	3.00	-0.32	-0.21		1.1
38.75	0.90	0.10	3.00	-0.58	-0.79	5.8	0
40.75	0.90	1.70	3.00	0.29	-0.50		
42.25	0.90	8.60	3.00	2.08	1.58	7.8	0
46.75	0.90	7.50	3.00	5.35	6.92	8.3	0
56.25	0.90	4.30	3.00	5.81	12.74	7	0
61.25	0.90	0.30	3.00	-0.54	12.20		0
64.25	0.90	0.10	3.00	-0.43	11.77	5.6	2.9
70.75	0.90	4.70	3.00	4.45	16.21	7.6	0
80.25	0.90	4.20	3.00	5.64	21.86	7.3	0
85.25	0.90	2.00	3.00	0.99	22.85	6.9	0
90.25	0.90	0.10	3.00	-0.72	22.13	7	2.7
95.75	0.90	0.30	3.20	-0.63	21.49	7.8	0
106.50	0.90	0.10	3.20	-1.65	19.84	7.8	6.9
111.50	0.90	0.10	3.20	-0.77	19.07	8.2	8
120.50	0.90	0.30	3.00	-0.97	18.10	7.6	0
128.50	0.90	3.10	3.00	3.17	21.27	7.3	0
130.75	0.90	2.00	3.00	0.45	21.71		0
133.50	0.90	1.20	3.00	0.15	21.86	8.1	0
135.00	0.90	0.70	3.00	-0.05	21.81		0
135.75	0.90	0.60	3.00	-0.04	21.77		0
138.08	0.90	0.10	3.00	-0.34	21.43	6.8	1.4
142.83	0.90	3.00	2.90	1.74	23.17	7.5	0
151.91	0.90	2.30	2.90	2.21	25.38	6.4	0
154.41	0.90	1.50	2.90	0.26	25.64		
157.00	0.90	0.80	2.90	-0.05	25.60	6.4	0
157.91	0.90	0.60	2.90	-0.05	25.55		
160.41	0.90	0.20	3.00	-0.32	25.23	6.9	2.5
165.07	0.90	5.90	3.00	4.19	29.43	6.9	0
174.41	0.90	4.10	2.80	5.02	34.45	6.9	0
176.33	0.90	3.10	3.10	0.79	35.23		
178.00	0.90	2.50	3.20	0.51	35.75	6.4	0
185.25	0.90	0.30	3.00	-0.78	34.96	7.1	1.4
189.42	0.90	2.00	3.00	0.83	35.79	5.6	0
200.42	0.90	6.30	2.80	9.98	45.77	6.8	0
203.92	0.90	4.80	2.90	2.38	48.14	7.2	0
208.50	0.90	1.90	3.00	0.82	48.97	8.7	0
211.58	0.90	0.50	3.00	-0.22	48.75	8.7	0
213.08	1.30	0.20	3.00	-0.30	48.45	8	2.2

Table A2 (con'd): Run# II-4 Data

Time (hours)	Inf. DO (mg/l)	Eff DO (mg/l)	Flow Rate ml/min	Oxygen trans (mg)	Cum O2 trans (mg)	Inf Xyl Conc (mg/l)	Eff Xyl Conc (mg/l) (hours)
222.25	1.00	3.00	2.90	3.19	51.64	7.9	0
226.75	1.00	4.60	3.00	2.92	54.56		
228.25	1.00	3.50	3.00	0.68	55.23		
233.25	1.00	1.00	3.00	0.00	55.23	6.4	0
236.42	1.00	0.10	3.00	-0.51	54.72	6.4	1.9
247.50	1.00	1.50	3.00	1.00	55.72	7.4	0
248.50	1.00	4.20	2.90	0.56	56.27		
250.25	1.00	3.10	2.90	0.64	56.91	7.8	0
256.25	1.00	0.10	3.20	-1.04	55.88	7.9	5.2
273.00	1.00	0.10	3.00	-2.71	53.16	7.9	7.3
277.00	1.00	0.10	3.00	-0.65	52.51		
282.17	1.00	4.10	3.00	2.88	55.40	7.6	0
296.50	1.00	3.00	3.00	5.16	60.56	8.3	0
301.83	1.10	0.10	3.00	-0.96	59.60	7.5	4.5
305.75	1.10	7.40	3.00	4.45	64.04	7.3	0
318.50	1.10	9.40	3.00	19.05	83.09	7.4	0
323.00	1.10	4.50	3.00	2.75	85.85	7.3	0
328.17	1.10	0.10	3.00	-0.93	84.92	7.1	4.1
331.75	1.10	0.10	3.00	-0.64	84.27	6.3	5.5
348.17	1.10	0.20	3.00	-2.66	81.61	7.3	5.5

Table A3: Run II-4 Data

Time (hours)	O2 used to bio xylene (mg)	Cum O2 used to bio xyl (mg)	Cum O2 trans + bio (mg)	Mano-meter 3 (in)	Mano-meter 5 (in)	ΔP (man3-man5) (in)	Kla (hr-1)
0	0	0	0	17.875	17.5	0.375	
8.50	2.754	2.754	1.53	17.875	17.625	0.25	
10.75	0	2.754	1.206	19	17.25	1.75	0.1856
13.50	12.42	15.174	14.121	19.0625	17.25	1.8125	0.2684
18.25	16.6725	31.8465	32.247			1.625	0.2630
22.75	16.281	48.1275	49.257	18.875	17.25	0.875	0.2314
32.50	35.2755	83.403	83.5146	18.125	17.25	0.875	0.1959
34.75	6.804	90.207	89.9946	18.125	17.25		0.2032
38.75	12.528	102.735	101.946		17.25	3	
40.75	0	102.735	102.234	20.25	17.25	2.5625	0.4309
42.25	14.742	117.477	119.055	19.8125	17.25	2.25	0.4288
46.75	20.169	137.646	144.570	19.5	17.25	1.5	0.3165
56.25	35.91	173.556	186.294	18.75	17.25	1.4375	0.2504
61.25	18.9	192.456	204.654	18.25	17.25	1	0.0894
64.25	4.374	196.83	208.596				0.3471
70.75	26.676	223.506	239.718		17.375		0.3264
80.25	37.449	260.955	282.810		17.375		0.2738
85.25	18.63	279.585	302.430		17.375		0.1481
90.25	11.61	291.195	313.320		17.375		0.2985
95.75	23.166	314.361	335.853		17.375		0.0248
106.50	5.2245	319.585	339.426		17.375		-0.0026
111.50	0.54	320.125	339.198		17.5625	2.375	0.2725
120.50	36.936	357.061	375.162	22.125	17.75	4.375	0.3073
128.50	31.536	388.597	409.866	20.75	17.625	3.125	0.2888
130.75	8.8695	397.467	419.181	20.3125	17.625	2.6875	0.3056
133.50	12.0285	409.495	431.358	20.125	17.625	2.5	0.2974
135.00	6.561	416.056	437.865			3.25	0.2957
135.75	3.2805	419.337	441.105	19.875	17.625	2.375	0.1885
138.08	6.79428	426.131	447.564	20.0625	17.6875	4.5	0.3028
142.83	19.2375	445.368	468.537	22.125	17.75	3.0625	0.2511
151.91	31.3804	476.749	502.129	20.625	17.5625	2.5625	
154.41	0	476.749	502.390			2.625	0.2281
157.00	17.5910	494.340	519.936	20	17.4375	4.5625	
157.91	0	494.340	519.880			2.9375	0.1532
160.41	8.10216	502.442	527.672	20.25	17.625	2.625	0.3413
165.07	17.3631	519.805	549.233	22	17.4375	2.375	0.2885
174.41	34.8008	554.606	589.055	20.3125	17.375	5.1875	
176.33	0	554.606	589.841	20.125	17.375	3.25125	0.2805
178.00	12.4070	567.013	602.761	20	17.375	3	0.2025
185.25	22.3155	589.329	624.293	21	18.625	2.625	0.2248
189.42	12.6100	601.939	637.729	22.9375	17.75	3.375	0.3218
200.42	40.392	642.331	688.100	20.5625	17.3112	3.25	0.3221
203.92	13.608	655.939	704.083	20.3125	17.3125	3.25	0.3398
208.50	21.5168	677.455	726.424	19.9375	17.3125	2.375	0.3163
211.58	14.4698	691.925	740.672	20.8125	17.4375	2.375	0.2009
213.08	4.698	696.623	745.073			2.3125	0.3168

Table A3: Run II-4 Data (con'd)

Time (hours)	O2 used to bio xylene (mg)	Cum O2 used to bio xyl (mg)	Cum O2 trans + bio (mg)	Mano-meter 5 (in)	Mano-meter 3 (in)	ΔP (man5-man3) (in)	Kla (hr-1)
222.25	39.1192	735.742	787.384	20.75	17.5	1.9375	
226.75	0	735.742	790.300	20.375	17.125	1.875	
228.25	0	735.742	790.975			1.875	
233.25	38.016	773.758	828.991	20	17.625	1.875	0.1544
236.42	7.7031	781.462	836.180	20.125	17.75	2.6875	0.2835
247.50	44.275	825.737	881.453	19.9375	17.625	1.5	
248.50	0	825.737	882.010				0.3147
250.25	11.583	837.320	894.233	19.5625	17.625	1.9375	0.0941
256.25	8.748	846.068	901.944	19.6875	17.8125	1.875	0.0110
273.00	5.427	851.495	904.657	20.375	18.5	1.875	
277.00	0	851.495	904.009	20.1875	18.3125	1.875	0.3354
282.17	37.6336	889.129	944.528	20.6875	18	2.6875	0.3430
296.50	64.2270	953.356	1013.91	19.6875	18.1875	1.5	0.0982
301.83	8.6346	961.991	1021.58	19.875	18.375	1.5	0.3843
305.75	15.4526	977.443	1041.48	20.0625	17.875	2.1875	0.4293
318.50	50.949	1028.39	1111.48	18.625	18	0.625	0.3300
323.00	17.739	1046.13	1131.97	19.125	18.0625	1.0625	0.0982
328.17	8.3754	1054.50	1139.42	19.25	18.0625	1.1875	0.0172
331.75	1.54656	1056.05	1140.32	19.25	18.25	1.0	0.0553
348.17	15.9602	1072.01	1153.62	21	19.875	1.125	0.2416

Table A4: Run III-6 Data

time (hours)	man2 (in)	man3 (in)	man5 (in)	man6 (in)	man3-man5 (in)	flow (ml/min)	inf DO (ppm)
0						3	0.1
10.33	26.25	24.75	21.5	20.5	3.25	3	0.1
14.083	30	29.375	23.4375	23	5.9375	2.8	0.1
16.083						3	0.1
17.83	27.875	26.8125	22.5	22.0625	4.3125	3	0.1
22.083	27.0625	26	22.375	21.875	3.625	3	0.1
32.083	26.75	25.625	22.875	22.375	2.75	3.1	0.1
35.83	27.75	27.5	20.375	20	7.125	2.9	0.1
38.83	25.75	25.1875	20.75	20.25	4.4375	2.9	0.1
41.83	25.5625	24.9375	21	20.5	3.9375	3	0.1
46.5	25.25	24.6875	21.25	20.6875	3.4375	3	0.1
56.083	24.3125	23.625	20.875	20.5	2.75	3	0.1
60.83	27.75	25.625	20.125	19.6875	5.5	3	0.1
66	25.4375	24.25	20	19.625	4.25	3.1	0.1
71.33	24.6875	23.5	20.3125	19.875	3.1875	3.1	0.1
80.83	25.375	23.75	21	20.5625	2.75	3.2	0.1
85.33	27.25	26.75	20.25	19.875	6.5	2.9	0.1
90.583	25.625	25.375	23.75	20.375	1.625	3	0.1
96.33	25.25	24.5	21.125	20.75	3.375	3.2	0.1
103.83	25.125	24.5	21.625	21.125	2.875	3	0.1
109.33	27.375	27.375	20.625	20.25	6.75	2.9	0.1
117.33	25.5	25.5	21.125	20.75	4.375	3	0.1
128.83	25	24.5	21.875	21.25	2.625	3	0.1
133.083	28.75	27.5625	22.625	21.75	4.9375	3	0.1
137.83	27.6875	25.25	21.3125	21	3.9375	2.7	0.1
142.67	27.6875	24.75	21.625	21.3125	3.125	2.8	0.1
152.83	25.25	24.75	22.125	21.875	2.625	3	0.1
160.083	27.75	26.8125	22.375	21.875	4.4375	2.8	0.1
165.83	27.3125	26.4375	22.875	22.4375	3.5625	3	0.1
176.83	27.875	26	23.8125	23	2.1875	3	0.1
179.33	23.1875	22.1875	20.125	19.6875	2.0625	3	0.1
190.083	24.5625	23.5	20	19.5	3.5	3.2	0.1
200.25	25.375	24.1875	21.625	21.125	2.5625	3	0.1
203.83	24.25	23.75	21.25	20.75	2.5	3	0.1
214.5	25.4375	24.375	20	19.625	4.375	3.2	0.1
224.33	24.25	23.125	20.125	19.6875	3	3.1	0.1
228.83	24.0625	23.125	20.25	19.875	2.875	3.1	0.1
238.583	27.625	26.625	20.75	20.3125	5.875	2.8	0.1
248.83						3.2	0.1
251.67						3.2	0.1
255.167						3.2	0.1
256.33	22.875	22.25	19.1875	18.6875	3.0625	3.2	0.1
263.5	22.75	22.125	18.4375	18	3.6875	3	0.1
276.83	21.375	20.875	18.625	18.125	2.25	3.2	0.1

Table A4 (con'd): Run III-6

time (hours)	man2 (in)	man3 (in)	man5 (in)	man6 (in)	man3-man5 (in)	flow (ml/min)	inf DO (ppm)
282.5	21.0625	20.5	18.375	17.875	2.125	3	0.1
286.33	23.9375	23.4375	18.6875		4.75	3.2	0.1
295.83	22.375	21.9375	18.875	18.375	3.0625	3	0.1
318.83	21.6875	21.3125	19.25	18.75	2.0625	3.1	0.1
332.83	23.125	22.5	18.875	18.125	3.625	3	0.2
342.33	22.125	22	19.25	18.875	2.75	3	0.2
345.16	22.125	22	19.25	18.875	2.75	3	0.2
351.33	24.9375	24.125	18.9375	18.5	5.1875	3	0.2
356.33	24.0625	23.375	19	18.625	4.375	2.9	0.2
367.83	21.9375	21.25	18.1875	17.875	3.0625	3	0.2
369.83						3	0.2
375.83	24.875	24.125	18	17.5	6.125	3	0.2
380.5	23.4375	22.875	17.8125	17.625	5.0625	3	0.2
390.8	21.75	21.125	17.9375	17.5625	3.1875	2.6	0.2
394.8						2.6	0.2
396.8						2.6	0.2
401.83	22.125	21.5	18.125	17.75	3.375	3	0.2

Table A5 : Run III-6

time (hours)	eff DO (ppm)	mg O2 trans	cum trans (mg O2)	xyl inf (ppm)	xyl eff (ppm)	O2 used to bio. xyl (mg)	cum O2 used to bio xyl (mg)
0	0.1	0	0	6.7	5.1	0	0
10.33	0.1	0	0	6.4	5.8	3.53657	3.53657
14.083	1.7	1.00880	1.00880	5.7	0	11.3925	14.9291
16.083	5.2	1.836	2.84480			6.50484	21.4339
17.83	5.3	1.63519	4.47999	5.7	0	5.68197	27.1159
22.083	3.7	2.75594	7.23594	5.7	0	13.8325	40.9485
32.083	0.1	0	7.23594			33.6083	74.5568
35.83	5.1	3.25989	10.4958	8.1	0	16.7408	91.2976
38.83	5.1	2.61	13.1058	5.8	0	9.59749	100.895
41.83	5.2	2.754	15.8598			9.92844	110.823
46.5	2.2	1.76526	17.6250	6.5	0	17.3205	128.144
56.083	0.1	0	17.6250	6.8	3.6	17.4977	145.641
60.83	6.2	5.21220	22.8372	6	0	16.2518	161.893
66	5	4.71193	27.5492	6.1	0	18.5948	180.488
71.33	2.3	2.18103	29.7302	7.8	0	24.5128	205.001
80.83	0.1	0	29.7302	8	3.7	24.8629	229.864
85.33	6.2	4.7763	34.5065	6.8	0	16.8783	246.742
90.583	4.8	4.44403	38.9506	6.4	0	19.1831	265.925
96.33	2.3	2.42753	41.3781	6	0	20.9871	286.913
103.83	0.1	0	41.3781	6.7	2.3	18.8298	305.742
109.33	6.1	5.742	47.1201	5.4	0	16.3819	322.124
117.33	3.7	5.184	52.3041	6.4	0	29.2147	351.339
128.83	0.1	0	52.3041	6.9	4.1	18.3733	369.712
133.083	6.9	5.20567	57.5098	9.6	0	23.2969	393.009
137.83	8	6.07521	63.5850	7.8	0	19.0146	412.024
142.67	5.1	4.0656	67.6506		0	20.1052	432.129
152.83	0.1	0	67.6506	6.5	0	37.6824	469.811
160.083	7.3	8.77322	76.4238	5.4	0	20.8583	490.670
165.83	5.4	5.48263	81.9064	6.6	0	21.6429	512.313
176.83	1	1.782	83.6884		0	41.4255	553.738
179.33	0.4	0.135	83.8234	6	0.8	7.4178	561.156
190.083	2.1	4.12915	87.9526	6	0	39.2682	600.424
200.25	1.3	2.19607	90.1487	6.1	0	35.3878	635.81
203.83	0.1	0	90.1487	6.2	2.9	6.74106	642.553
214.5	5.1	10.2432	100.391	5.4	0	35.0686	677.622
224.33	4.4	7.86203	108.253	5.3	0	30.7186	708.341
228.83	0.9	0.6696	108.923	5.4	0		722.668
238.583	5.5	8.84792	117.771	5.1	0	26.4896	749.158
248.83	3.8	7.27946	125.050	5.6	0	34.9257	784.084
251.67	3	1.58131	126.632			9.85266	793.936
255.167	1	0.60428	127.236			12.1319	806.068
256.33	0.6	0.11164	127.348	5.7	0	4.03473	810.103
263.5	9.2	11.7444	139.092	5.2	0	21.2742	831.377
276.83	1.4	3.32716	142.419	5.8	0	47.0563	878.434

Table A5 (con'd): Run III-6

time (hours)	eff DO (ppm)	mg O2 trans	cum trans (mg O2)	xyl inf (ppm)	xyl eff (ppm)	O2 used to bio. xyl (mg)	cum O2 used to bio xyl (mg)
282.5	0.100	0.000	142.420	5.800	4.100	5.500	883.934
286.33	8.200	5.956	148.376	7.000	0.000	16.318	900.252
295.83	5.800	9.747	158.123	4.500	0.000	24.393	924.645
318.83	0.100	0.000	158.123	4.200		56.957	981.602
332.83	1.800	4.032	162.155	5.000	0.000	39.942	1021.54
342.33	0.600	0.684	162.839	5.500	0.000	29.814	1051.35
345.16	0.100	-0.051	162.788		2.600	4.683	1056.04
351.33	6.800	7.330	170.118	5.200	0.000	18.307	1074.34
356.33	5.200	4.350	174.468	6.300	0.000	17.375	1091.72
367.83	0.800	1.242	175.710			41.340	1133.06
369.83	0.100	-0.036	175.674			7.190	1140.25
375.83	8.800	9.288	184.962			21.569	1161.82
380.5	7.600	6.220	191.183			16.788	1178.60
390.8	3.100	4.660	195.842	4.700	0.000	23.940	1202.54
394.8	2.100	1.186	197.028			9.297	1211.84
396.8	1.800	0.499	197.527			4.648	1216.49
401.83	0.500	0.272	197.799			13.490	1229.98

Table A6: Run III-6 Data

time (hours)	ferrous inf (ppm)	ferrous eff (ppm)	mg o2 oxidize ferrous	cum oxidize ferrous	tot.cum (trans+ bio+oxi) mg	Kla (hr-1)
0	11.3	11	0.000	0.000	0.000	
10.33	6.3	0.4	1.567	1.567	5.104	
14.083	8.5	1.2	.658	2.225	18.163	0.228
16.083	10.8	0	.555	2.780	27.059	0.309
17.83			.485	3.265	34.861	0.310
22.083	12.8	0	1.400	4.665	52.850	0.287
32.083	14.3	0.6	3.640	8.305	90.098	
35.83			1.276	9.581	111.375	0.392
38.83	13.5	0	1.007	10.588	124.589	0.305
41.83			1.041	11.630	138.313	0.318
46.5	13.8	1.7	1.453	13.083	158.852	0.291
56.083	15	7.6	1.824	14.906	178.173	
60.83	15	1.2	1.685	16.591	201.322	0.344
66	14.3	0	1.964	18.555	226.593	0.338
71.33	12.8	1.5	1.600	20.155	254.887	0.351
80.83	12.6	6	1.720	21.875	281.470	
85.33		1.2	1.275	23.150	304.400	0.359
90.583	13.8	1.7	1.634	24.785	329.661	0.331
96.33	15	2.8	1.923	26.708	354.999	0.292
103.83	13.4	7.7	1.099	27.807	374.928	
109.33	13.4	1.7	1.600	29.407	398.652	0.304
117.33	0	2.2	-.453	28.954	432.598	0.286
128.83	0	0	.000	28.954	450.971	
133.083	8.8	0	.962	29.917	480.436	0.492
137.83	10.4	0	1.143	31.059	506.669	0.400
142.67	12	0	1.394	32.453	532.233	0.365
152.83	13.4	5.8	1.986	34.439	571.901	
160.083	10.8	1.3	1.654	36.092	603.187	0.310
165.83	11.4	1.6	1.448	37.541	631.760	0.346
176.83		2.1	2.631	40.171	677.599	0.270
179.33	1.3	0	.084	40.255	685.235	0.196
190.083			.383	40.638	729.016	0.268
200.25	0.6	0	.157	40.795	766.757	0.241
203.83	0	0	.000	40.795	773.498	
214.5	10.2	0	2.985	43.780	821.795	0.314
224.33	11.2	0	2.925	46.706	863.301	0.289
228.83	12	1.6	1.244	47.949	879.542	0.234
238.583	12.4	0	2.902	50.852	917.782	0.274
248.83	9.7	0	2.726	53.578	962.713	0.297
251.67			.756	54.334	974.903	0.287
255.167	10.6	2.4	.787	55.120	988.425	0.251
256.33			.262	55.382	992.833	0.244
263.5	9.6	0	1.770	57.152	1027.62	0.361
276.83	10.2	1.4	3.217	60.369	1081.22	0.262

Table A6 (con'd): Run III-6

time (hours)	ferrous inf (ppm)	ferrous eff (ppm)	mg o2 oxidize ferrous	cum oxidize ferrous	tot.cum (trans+ bio+oxi) mg	Kla (hr-1)
282.5	10	3.8	0.904	61.273	1087.62	
286.33	11.2	0	1.177	62.450	1111.07	0.446
295.83	10.4	0.6	2.394	64.844	1147.61	0.270
318.83		8	1.467	66.310	1206.03	
332.83	12	1.1	3.924	70.234	1253.93	0.225
342.33	11.4	0.8	2.589	72.824	1287.02	0.225
345.16	11.4	1.1	0.750	73.573	1292.40	0.122
351.33			1.634	75.207	1319.67	0.316
356.33			1.280	76.488	1342.67	0.319
367.83			3.046	79.533	1388.30	0.257
369.83			0.530	80.063	1395.99	0.246
375.83			1.589	81.652	1428.43	0.399
380.5			1.237	82.889	1452.68	0.375
390.8	11	1.4	2.204	85.093	1483.48	0.201
394.8			0.856	85.949	1494.82	0.188
396.8			0.428	86.376	1500.39	0.184
401.83			1.242	87.618	1515.40	0.192

Table A7: Run IV-7 Data

Time (hours)	man2 (in)	man3 (in)	man5 (in)	man6 (in)	man3-man5 (in)	flow (ml/min)	inf DO (ppm)
0	22.75	21.625	18.625	18.4375	3	3	0.2
12.08						3	0.2
18.33	24	31.875	19.375	18.875	12.5	3.1	0.2
36.83	23	22.4375	19.75	19.25	2.6875	3.2	0.2
38.33						3	0.2
41.67	22.625	22.5625	19.625	19.1875	2.9375	3	0.2
48.58	23.6875	23.125	19.3125	18.8125	3.8125	3.2	0.2
61.08		22.0625	19.3125	18.875	2.75	2.9	0.2
64.08						2.9	0.2
68.5						2.9	0.2
69.5	22.625	22.125	19.75	19.25	2.375	3	0.2
83.33						3	0.2
85.33	21.3125		18.1875	17.8125		2.9	0.2
94.33	20.9375	20.5	18.375	17.9375	2.125	3	0.2
107.33	20.4375	19.875	18.5	18	1.375	2.9	0.2
113.58	20.9375	20.6875	18.625	18.125	2.0625	3	0.2
119.33	20.9375	20.75	18.8125	18.3125	1.9375	3	0.2
130.33	21.375	21.0625	19.1875	18.75	1.875	2.9	0.2
139.83			18.625	18.125		3	0.2
143.92	20.9375		18.6875	18.1875		3.2	0.2
155	20.875	20.5	18.875	18.375	1.625	3.1	0.2
161.83	21.375	20.4375	18.5	18.0625	1.9375	2.8	0.2
182.08	21.25	20.325	19	18.5	1.325	2.9	0.2
186.42	22.75	22.75	19.25	18.75	3.5	3	0.2
192	22.25	21.6875	18.9375	18.4375	2.75	3.2	0.2
201.58	21.6875	21.125	19.125	18.5	2.0	3.1	0.2
204.33						3.1	0.2
207.33						3.1	0.2
208.83	21.25	20.75	18.9375	18.3125	1.8125	3.1	0.2
211.58						3.1	0.2
215.58						3.1	0.2
227.33	21.75	21.3125	18.75	18.25	2.5625	3	0.2
231.67						3	0.2
233.33		20.6875	18.375	17.875	2.3125	3	0.2
240	22.25	21.4375	19.25	18.625	2.1875	4.1	0.2
251	23.125	21.875	19.625	19	2.25	3.9	0.2
258.08	26.6875	24.0625	20.25	19.5625	3.8125	4.4	0.2
273.58	24.75	22.6875	19.75	19.1875	2.9375	4.4	0.2
282.08	27.0625	24.875	20.3125	19.625	4.5625	4.1	0.2
287.33	26.25	24	20.25	19.8125	3.75	4.2	0.2
297.58	27	24.5	21.125	20.625	3.375	4.2	0.2
303.58	27.4375	26.75	21.3125	20.625	5.4375	4.3	0.2
311.5	28.6875	25.625	21.625	21	4	4.3	0.2
316.3	27.4375	26.75	21.3125	20.625	5.4375	4	0.2

Table A7 (con'd): Run IV-7

Time (hours)	man2 (in)	man3 (in)	man5 (in)	man6 (in)	man3-man5 (in)	flow (ml/min)	inf DO (ppm)
329.58	30.625	27.75	23.875	23.25	3.875	4.3	0.2
347.58						4.4	0.2
359.58						4.4	0.2
370.58						4.4	0.7
393.33		25.375	22.0625	21.1875	3.3125	4.6	0.7
405.58	29.0625	25.375	22.4375	21.5625	2.9375	4.2	0.7
411.83	31.9375	27.6875	23.875	23.125	3.8125	4.2	0.7
419.58	31.0625	27.5	24.5625	23.6875	2.9375	4.2	0.7
431.08	32.5	29.8125	27.375	26.625	2.4375	4.2	0.7

Table A8: Run IV-7 Data

Time (hours)	eff DO (ppm)	mg O2 trans	cum trans (mg O2)	xyl inf (ppm)	xyl eff (ppm)	O2 used to bio. xyl (mg)	cum O2 used to bio xyl (mg)
0	0.1	-.066	-.066	4.7	0	9.842	9.842
12.08	0.1	-.217	-.284	4.7	0	6.893	16.735
18.33	8	9.068	8.784	4.2	0	4.422	21.157
36.83	1.4	4.262	13.046	5	0	20.268	41.425
38.33	1	.216	13.262	5	0	1.541	42.966
41.67	0.2	.000	13.262	5	0	4.193	47.158
48.58	7.3	9.420	22.682	6	0	9.253	56.411
61.08	2.6	5.220	27.902	5	0	19.305	75.716
64.08	1.3	.574	28.476	5	0	4.633	80.349
68.5	0.5	.231	28.707	5	0	6.826	87.176
69.5	0.1	-.018	28.689	5	0	1.598	88.774
83.33	5.8	13.941	42.630	5	0	22.096	110.869
85.33	4.4	1.462	44.091	7.2	0	4.633	115.503
94.33	0.3	.162	44.253	7.2	0	16.433	131.936
107.33	6.8	14.929	59.182	6.1	0	22.946	154.882
113.58	2.1	2.138	61.320	6.1	0	.000	154.882
119.33	0.1	-.104	61.216	6.8	2.3	-7.546	147.336
130.33	0.1	-.191	61.025	6.2	2.7	7.281	154.616
139.83	9.4	15.732	76.757	4.8	0	5.963	160.579
143.92	6.5	4.947	81.704	4.8	0	5.228	165.807
155	0.1	-.206	81.498	4.8	2.6	15.026	180.833
161.83	9.1	10.212	91.710	5.1	0	3.637	184.470
182.08	0.1	-.352	91.358	5.6	2.1	7.819	192.289
186.42	10	7.656	99.014	4.3	0	.000	192.289
192	9.8	10.285	109.299	4.1	0	.000	192.289
201.58	5	8.553	117.852	8.6	0	22.594	214.883
204.33	3.1	1.483	119.335	8.6	0	6.486	221.369
207.33	1.5	.725	120.061	8.6	0	7.075	228.444
208.83	0.3	.028	120.089	8.6	0	.000	228.444
211.58	0.1	-.051	120.037	8.6	0	.000	228.444
215.58	7.1	5.134	125.171	6.3	0	.000	228.444
227.33	7.1	14.594	139.765	7.3	0	21.455	249.899
231.67	4.5	3.359	143.124	7.3	0	.000	249.899
233.33	3.5	.986	144.110	8.9	0	3.694	253.593
240	0.1	-.164	143.946	9.5	0	40.051	293.644
251	0.1	-.257	143.688	9.3	5.7	6.528	300.171
258.08	6.2	11.215	154.903	6.4	0	30.218	330.389
273.58	0.1	-.409	154.494	6.4	3.6	19.457	349.847
282.08	4.5	8.991	163.485	5.5	0	25.851	375.698
287.33	1.7	1.985	165.470	5.6	0	16.776	392.473
297.58	0.1	-.258	165.211	7.7	0	33.571	426.045
301.58	4.8	4.747	169.958	4.1	0	10.469	436.513
311.5	1.6	2.861	172.819	4.4	0	20.728	457.241
316.3	7.4	11.750	184.570	5	0	11.899	469.140

Table A8 (con'd): IV-7

Time (hours)	eff DO (ppm)	mg O2 trans	cum trans (mg O2)	xyl inf (ppm)	xyl eff (ppm)	O2 used to bio. xyl (mg)	cum O2 used to bio xyl (mg)
329.58	0.1	-.343	184.227	4	2.6	-11.947	457.193
347.58	0.1	-.475	183.752	4.3	1.8	.000	457.193
359.58	0.1	-.317	183.435	2.3	1.8	.000	457.193
370.58	6	15.391	198.826	2.3	1.8	.000	457.193
393.33	3.1	15.070	213.896	4.3	0	47.771	504.963
405.58	0.1	-1.852	212.044	4.3	2.4	1.957	506.921
411.83	6.6	9.293	221.336	3.7	0	12.482	519.402
419.58	2.5	3.515	224.851	2.3	0	14.239	533.642
431.08	0.1	-1.739	223.113	3.1	0	27.560	561.202

Table A9: Run IV-7 Data

Time (hours)	ferrous inf (ppm)	ferrous eff (ppm)	mg o2 oxidize ferrous	cum oxidize ferrous	tot.cum (trans+ bio+oxi) mg	Kla (hr-1)	Xylene Pre-bio (ppm)	Ferrous Pre-bio (ppm)
0			.906	.906	10.682	.186		
12.08	8.6	5	2.982	3.888	20.340	.150	1	6.1
18.33	7.2	0	1.196	5.084	35.025	.250	1.2	5.9
36.83	7.3	0	3.704	8.788	63.259	.156	1.8	7.3
38.33			.282	9.070	65.298	.140	1.8	
41.67	10.2	3.5	.575	9.645	70.066		2.2	
48.58	10.2	0	1.933	11.578	90.671	.286	2.2	
61.08	10.2	1.4	2.734	14.312	117.931	.124	2.8	10.2
64.08			.656	14.969	123.794	.107	2.8	
68.5			.967	15.936	131.818	.096	2.8	
69.5			.226	16.162	133.624	.094	2.8	
83.33			3.627	19.789	173.288	.179	2.8	
85.33	11.9	1.8	.502	20.291	179.885	.182	4.2	13.3
94.33		5.4	1.504	21.796	197.985	.158	3.2	12.8
107.33	10.3	0.6	3.134	24.930	238.994	.215	3.2	
113.58	10.2	0	1.639	26.569	242.771	.270	0	1.7
119.33	8	3.2	.710	27.279	235.831	.255	0	
130.33	10.6	6.4	1.148	28.428	244.069	.087	3.9	13.0
139.83	8.6	0	2.199	30.626	267.962	.300	1.1	11.5
143.92		1	.897	31.524	279.035	.220	2.1	
155	13.2	6.6	1.943	33.467	295.798	.007	4.9	14.7
161.83	13.6	0	2.229	35.696	311.876	.299	1	7.3
182.08	8.9	7.5	.705	36.401	320.047	.100	2.8	
186.42	10.8	0	1.205	37.606	328.909	.340	0	6.3
192	9.4		1.439	39.045	340.632	.347	0	7.2
201.58	9.6		2.444	41.488	374.223	.268	4	10
204.33			.701	42.190	382.894	.236	4	
207.33			.765	42.955	391.460	.210	4	
208.83	9.6		.383	43.338	391.871	.343	0	11
211.58			.701	44.039	392.521	.339	0	
215.58	10.5	0	1.116	45.155	398.770	.378	0	9.8
227.33	10		3.021	48.177	437.840	.276	3.2	9.7
231.67			1.116	49.293	442.315	.356	0	
233.33	10.6	0	.452	49.745	447.448	.252	3.9	11.2
240	7.2		1.688	51.433	489.022	.105	7.7	9.8
251	9.8		3.604	55.036	498.896	.153	6.5	7.2
258.08	9	2	1.869	56.906	542.198	.211	5.1	9.2
273.58	9.6	6.7	1.695	58.601	562.941	.075	5.1	7.0
282.08	9.6	2	2.270	60.871	600.054	.179	3.9	10.2
287.33	11.5		2.174	63.045	620.988	.138	4	10.2
297.58	6.8		2.509	65.554	656.810	.198	4.1	7.9
301.58	10.6		1.563	67.116	673.588	.164	3.2	5.9
309.5		2	2.510	69.627	699.687	.110	3.2	7.0
316.3	7.9		1.842	71.469	725.178	.295	2.3	7.3

Table A9 (con'd): Run IV-7 Data

Time (hours)	ferrous inf (ppm)	ferrous eff (ppm)	mg o2 oxidize ferrous	cum. oxidize ferrous (mg)	tot.cum (trans+ bio+oxi) mg	Kla (hr-1)	Xylene Pre-bio (ppm)	Ferrous Pre-bio (ppm)
329.58			2.300	73.769	715.189	.140	1.5	7.6
347.58	9.6	4.9	6.517	80.286	721.231	.156	1.8	7.6
359.58			.091	80.377	721.004	.025	1.8	7.6
370.58	6.7	6.5	3.153	83.530	739.549	.153	1.8	7.3
393.33	7.6	0	5.382	88.912	807.771	.175	2.4	7.1
405.58		1.6	3.352	92.263	811.227	.095	2.6	5.7
411.83		0	2.093	94.356	835.094	.203	2.5	4.6
419.58	9.3		2.595	96.950	855.444	.055	2.3	4.4
431.08	9.3		3.850	100.801	885.115	.018	3	4

Table A10: CGA Injection Data

	ml oxygen	quality (%)	flow rate (ml/ min)	length of inj. (sec)	
run II-1	125	65	278	42	
run II-2	125	64	304	38.5	
run II-3	125	64	277	42	
run II-4	125	68	240	46	
	125	66	238	48	
	125	67	228	49	
	?	67	234	48	O2 flow stopped during preparation of CGA
	62.5	71	237	22	Actual length= 30 sec
	100	68	231	38.2	
	110	69	241	40	
	125	69	219	50	
	110	69	208	38	
	75	66	220	31	
	85	67	231	33	
	110	66	226	44	
average run II-4	104.772	67.8181	229		
avg run II-4 (mg O2)	139.473				
run III-6	115	63	125	88	
	115	63	183	60	
	115	63	177	61	
	115	66	175	60	
	115	64	196	55	
	115	64	159	68	
	115	60	181	64	
	115	60	171	68	
	115	63	186	59	
	115	62	181	62	
	115	63	160	68	
	115	66	151	69	
	115	62	156	72	
	115	62	154	73	
	115	62	145	77	
average runIII-6	115	62.86	166.66		
Avg run III-6 (mgO2)	153.088				

Table A10 (con'd): CGA Injection Data

	ml oxygen	quality (%)	flow rate (ml/ min)	length of inj. (sec)	
run IV-7	115	62	147	76	
	100	66	171	53	
	100	67	161	56	
	100	62	158	62	
	100	62	163	60	
	100	63	152	63	
	100	64	139	68	
	100	65	174	53	Actual length = 60 sec
	100	61	140	70	
	100	62	160	60	
	100	63	166	57	
	100	64	154	61	
	100	64	149	63	
	100	64	152	60	
average run IV-7	101.071	63.5	156.142		
Avg run IV-7 (mg O2)	134.546				

Appendix B:

Sample Calculations

Sample calculations are for Run III-6 at time = 22.083, data can be found in Tables A4, A5, and A6.

Oxygen dissolved in flowing ground water (Od):

O_d (mg) = ΔT (DO_e-DO_i) Q (60 min/h) (10^{-3} l/ml)

ΔT = time between readings (h)
DO_e = effluent dissolved oxygen concentration (mg/l)
DO_i = inluent dissolved oxygen concentration (mg/l)
Q = flow rate (ml/min)

$O_d = (22.083-17.83)(3.7-0.1)(3.0)(60)10^{-3} = 2.756$ mg

Oxygen requirement for xylene biodegradation:

$C_8H_{10} + 10.5\ O_2 = 8CO_2 + 5H_2O$

$$\left(\frac{10.5 \text{ mole } O_2}{1 \text{ mole } C_8H_{10}}\right)\left(\frac{\text{mole } C_8H_{10}}{106.17 \text{ g } C_8H_{10}}\right)\left(\frac{32 \text{ g } O_2}{\text{mole } O_2}\right) = 3.165 \left(\frac{\text{g } O_2}{\text{g } C_8H_{10}}\right)$$

Oxygen utilized for xylene biodegradation (O_x):

$O_x = \Delta T(X_i - X_e)Q(60 \text{ min/h})(10^{-3} \text{ l/ml})(3.17 \text{ mg } O_2/\text{mg xylene})$

X_i = influent xylene concentration (mg/l)
X_e = effluent xylene concentration (mg/l)

$O_x = (22.083-17.83)(5.7-0)(3)(60)(10^{-3})3.17 = 13.83$ mg

Oxygen requirement for ferrous oxidation:

$4Fe(NH_4)_2SO_4 \cdot 6H_2O + O_2 = 4Fe(OH)_3 + 14H_2O + 4H_2(NH_4)_2SO_4$

$$\left(\frac{4 \text{ moles Fe}}{1 \text{ mole } O_2}\right)\left(\frac{\text{mole } O_2}{32 \text{ g}}\right)\left(\frac{55.847 \text{ g}}{\text{mole Fe}}\right) = 6.98 \left(\frac{\text{g } Fe^{++}}{\text{g } O_2}\right)$$

Oxygen utilized for ferrous oxidation(Of):

O_f (mg)= $\Delta T(F_i - F_e)Q(60\ min/h)(10^{-3}\ l/ml)(1\ mg\ O_2/7\ mg\ Fe)$

$O_f = (22.083 - 17.83)(12.8-0)(3)(60)(10^{-3})(1/7) = 1.40$ mg

Oxygen Mass Transfer Coefficient (K_1a)

$$L\ (X_2-X_1) = K_1a\ Z\ (X_A - X_{A,L})$$

where: Kla = mass transfer coefficient (hr-1)

$$or = \frac{\frac{mg}{l\ hr}\ O_2 \text{ dissolved in liquid phase}}{\frac{mg}{l}\ O_2 \text{ driving force}}$$

$X_A - X_{A,L}$ = log mean driving force

$$= \frac{(C_s-X_1) - (C_s-X_2)}{\ln \frac{C_s-X_1}{C_s-X_2}}$$

C_s = Saturation conc.of O_2 in water (mg/l)

$$K_1a\ (hr^{-1}) = \frac{L[DO_i-DO_e + (X_i-X_e)3.17\ \frac{mg\ O_2}{mg\ xyl} + (F_i-F_e)0.14\ \frac{mg\ O_2}{mg\ Fe}]}{Z\ \frac{(C_s-DO_i) - (C_s-DO_e)}{\ln \frac{C_s-DO_i}{C_s-DO_e}}}$$

Z = zone across which oxygen transfer is occurring = 4" = 10.2 cm

L (cm/h) = Q/A

$$A = \text{column area} = \frac{\pi\ 2.75^2\ in^2}{4}\ \frac{12^2\ in^2}{30.48^2\ cm^2} = 38.32\ cm^2$$

$$Q = \frac{3\ cm^3}{min}\ \frac{1}{38.32\ cm^2}\ \frac{60\ min}{hr} = 4.697\ \frac{cm}{hr}$$

$$Kla = \frac{4.697\ [3.7-0.1 + (5.7-0)\ 3.17 + (12.8-0)\ 0.14\ ]}{10.2\ \frac{(38.3 - 0.1) - (38.3 - 3.7)}{\ln \frac{38.3 - 0.1}{38.3 - 3.7}}} = 0.285\ hr^{-1}$$

Oxygen required for surfactant biodegradation:

Tergitol ($C_{39}H_{80}O_{14}$):

$$C_{39}H_{80}O_{13} + 52\ O_2 = 39\ CO_2 + 40\ H_2O$$

$$\frac{\text{mole } C_{39}H_{80}O_{14}}{52 \text{ mole } O_2}\ \frac{772 \text{ g}}{\text{mole } C_{39}H_{80}O_{14}}\ \frac{\text{mole } O_2}{32 \text{ g}} = 0.464\ \frac{\text{g tergitol}}{\text{g } O_2}$$

NaDBS ($NaC_{21}H_{35}SO_4$):

$$NaC_{21}H_{35}SO_4 + 29.75\ O_2 = 21\ CO_2 + 17.5\ H_2O + NaSO_4$$

$$\frac{\text{mole } NaC_{21}H_{35}SO_4}{29.75 \text{ mole O2}}\ \frac{374.5 \text{ g}}{\text{mole}}\ \frac{\text{mole O2}}{32 \text{ g}} = 0.394\ \frac{\text{g NaDBS}}{\text{g O2}}$$

For a solution of 75% Tergitol 25% NaDBS:

$$0.75\ (0.464) + 0.25\ (0.394) = 0.447\ \frac{\text{g surfactant}}{\text{g } O_2}$$

$$\text{or } 2.24\ \frac{\text{g O2}}{\text{g surfactant}}$$

For a CGA solution that is 65% oxygen and 150 ppm surfactant:

$$\frac{2.24 \text{ g } O_2}{\text{g surfactant}}\ \frac{150 \text{ mg surf}}{1 \text{ } H_2O}\ \frac{\text{g}}{10^3 \text{ mg}}(0.35 \text{ l } H_2O)\frac{\text{mole } O_2}{32 \text{ g}}\ \frac{1 \text{ } O_2}{0.0416 \text{ mol } O_2}$$

= 0.0883 l of oxygen required for surfactant biodegradation

$$\frac{0.0883 \text{ l } O_2 \text{ required}}{0.65 \text{ l } O_2 \text{ injected}} = 0.136$$

or 13.6% of injected oxygen will contribute to surfactant biodegradation

Appendix C: Miscellaneous Graphs

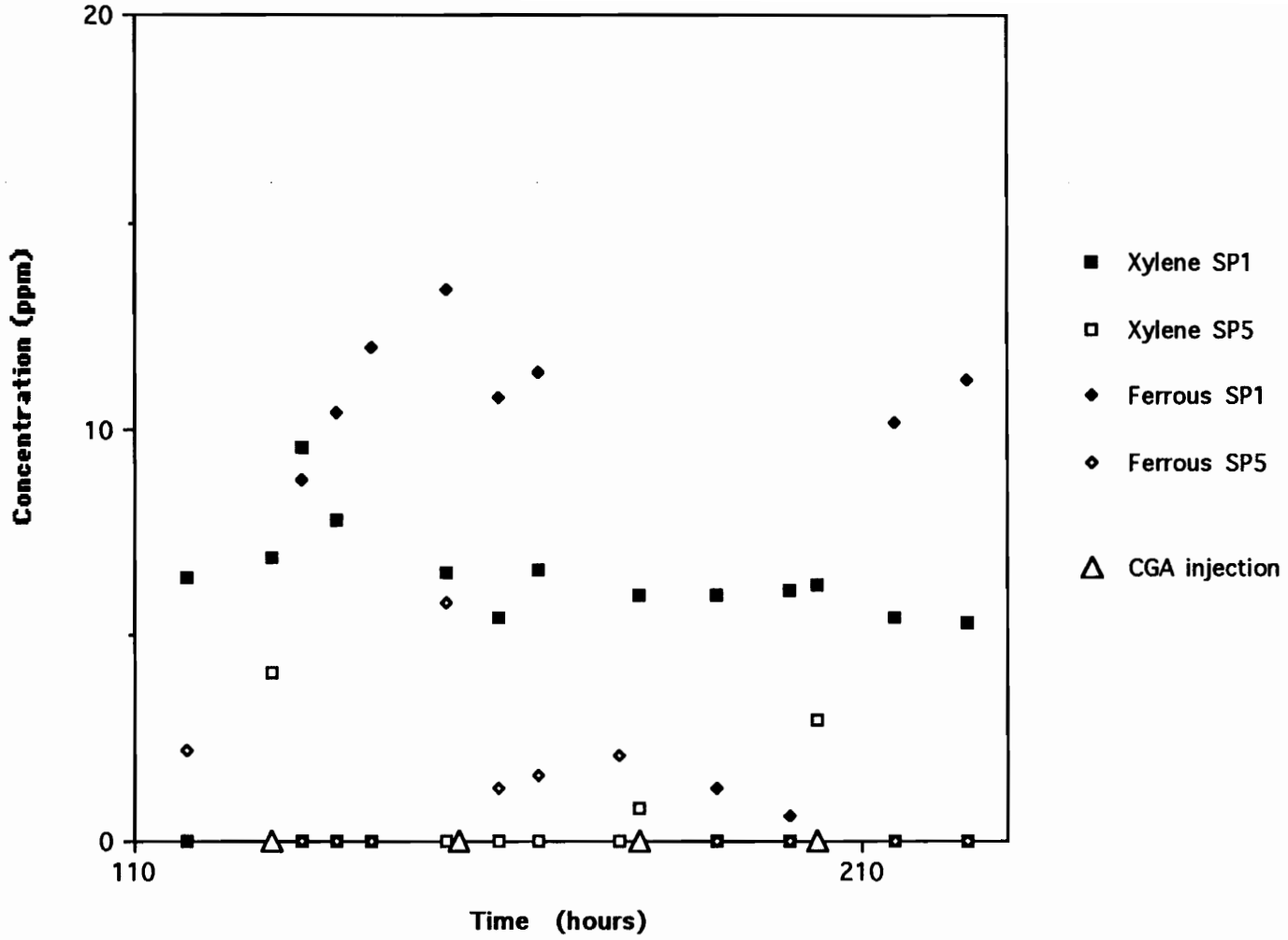

Figure C1: Xylene and Ferrous Concentrations - 2

VCTC - Run III-6

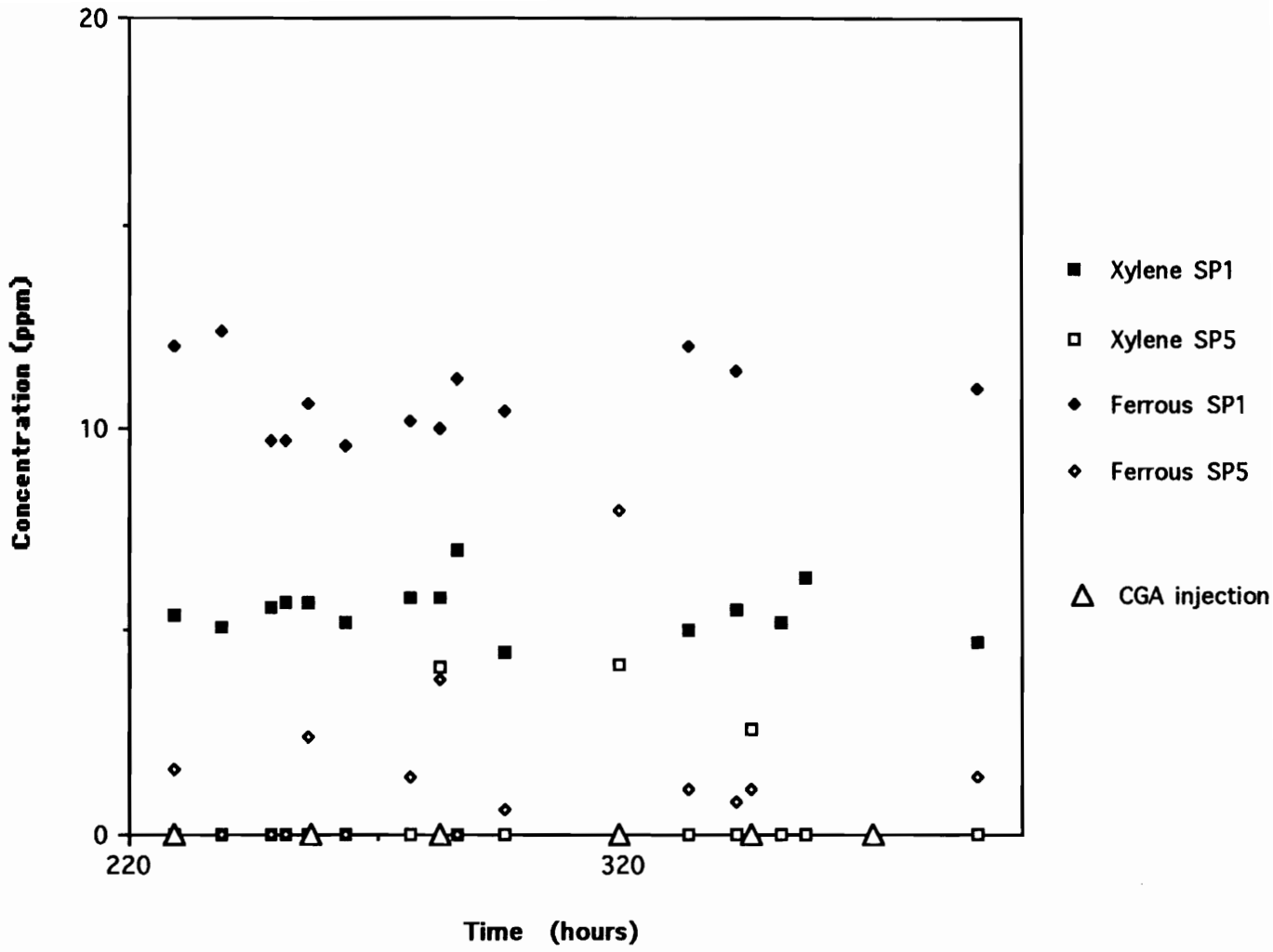

Figure C2: Xylene and Ferrous Concentrations - 3

VCTC - Run III-6

VITA

Kristen Buch Jenkins was born on December 22, 1967 in Kingsport, TN. She attended elementary and middle school in Columbia, South Carolina and high school in Kingsport, Tennessee. After graduating, she enrolled at the University of Tennessee in Knoxville, where she received her Bachelor of Science degree in Chemical Engineering in May 1990. After graduation she started work on a Master's degree in Chemical Engineering from Virginia Polytechnic Institute and State University. Following graduation, she will start working for Texaco Research and Development in Port Arthur, Texas.

Her mother, Betty Buch Jenkins, resides in West Point, Virginia and her brother, William Clinton Jenkins, III, (Jay), is attending East Carolina University.