Final Report:
Hopewell Beneficial CO_2 Capture for Production of Fuels, Fertilizer and Energy
Honeywell Hopewell Resin & Chemicals Plant
Hopewell, VA

Technical Report	**Final Report**
Reporting Period Start Date:	**Jan 15th, 2010**
Reporting Period End Date:	**Sept 30th, 2010**
Principal Author(s):	**Steve Lupton** **UOP LLC**
Date Report was issued:	**Jan 26th, 2011**
DOE Award Number:	**DE-FE0002568**

Name and Address of Submitting Organizations:

UOP LLC, 25. E. Algonquin Rd, Des Plaines, IL, 60016

Honeywell Resins & Chemicals, 905 E. Randolph Rd., Hopewell, VA, 23860

Honeywell Process Solutions, 2500 W. Union Hills Dr., Phoenix, AZ, 85027

Aquaflow Bionomics Ltd, PO Box 3295, Richmond, Nelson, New Zealand

DISCLAIMER

ABSTRACT

For Phase 1 of this project, the Hopewell team developed a detailed design for the Small Scale Pilot-Scale Algal CO_2 Sequestration System. This pilot consisted of six (6) x 135 gallon cultivation tanks including systems for CO_2 delivery and control, algal cultivation, and algal harvesting. A feed tank supplied Hopewell wastewater to the tanks and a receiver tank collected the effluent from the algal cultivation system. The effect of environmental parameters and nutrient loading on CO_2 uptake and sequestration into biomass were determined. Additionally the cost of capturing CO_2 from an industrial stack emission at both pilot and full-scale was determined. The engineering estimate evaluated Amine Guard technology for capture of pure CO_2 and direct stack gas capture and compression. The study concluded that Amine Guard technology has lower life-cycle cost at commercial scale, although the cost of direct stack gas capture is lower at the pilot scale.

Experiments conducted under high concentrations of dissolved CO_2 did not demonstrate enhanced algae growth rate. This result suggests that the dissolved CO_2 concentration at neutral pH was already above the limiting value. Even though dissolved CO_2 did not show a positive effect on biomass growth, controlling its value at a constant set-point during daylight hours can be beneficial in an algae cultivation stage with high algae biomass concentration to maximize the rate of CO_2 uptake.

The limited enhancement of algal growth by CO_2 addition to Hopewell wastewater was due at least in part to the high endogenous CO_2 evolution from bacterial degradation of dissolved organic carbon present at high levels in the wastewater. It was found that the high level of bacterial activity was somewhat inhibitory to algal growth in the Hopewell wastewater.

The project demonstrated that the Honeywell automation and control system, in combination with the accuracy of the online pH, dissolved O_2, dissolved CO_2, turbidity, Chlorophyll A and conductivity sensors is suitable for process control of algae cultivation in an open pond systems.

This project concluded that the Hopewell wastewater is very suitable for algal cultivation but the potential for significant CO_2 sequestration from the plant stack gas emissions was minimal due to the high endogenous CO_2 generation in the wastewater from the organic wastewater content. Algae cultivation was found to be promising, however, for nitrogen remediation in the Hopewell wastewater.

EXECUTIVE SUMMARY

The goal of this project was to assess the capture of stack gas from the Kellogg ammonia plant at Honeywell's Hopewell plant and the use of this stack gas to directly supply carbon dioxide to an algal cultivation system using sparging through fine bubble diffusers. The algal cultivation system was evaluated as a mechanism to treat process wastewater generated by the plant, which is rich in nitrogen contaminants. The ability of CO_2 present in the stack gas to promote the growth of algae and the incorporation of the nitrogen contaminants into the algal biomass was evaluated. The utility of algal biomass harvested from the cultivation ponds as a feedstock for fuel and power generation via biomass liquefaction and pyrolysis was also evaluated.

Wastewater was collected from the discharge of process wastewater into the plant equilibration ponds and transported in tote tanks to the site of the pilot. The pilot system consisted of six (6) x 135 gallon cultivation tanks including a CO_2 delivery and control system designed for algal cultivation. Process wastewater was fed to the algal cultivation tanks. Critical parameters such as pH, dissolved CO_2, biomass concentration and total nitrogen levels were monitored, with CO_2 and caustic addition controlled by a DCS system to ensure optimal algal growth conditions.

The engineering analysis of CO_2 capture was conducted by the UOP Gas Processing group to determine the most economical process for the delivery of CO_2 to an algal cultivation system both at pilot scale and at full-scale. This engineering analysis indicated that for the pilot scale envisioned for Phase 2 of this project, the capture of pure CO_2 from the stack gas using an Amine Guard system was significantly more expensive in both capital and operating expenses compared to direct stack gas compression. The engineering study concluded that the most cost effective method of supplying CO_2 to the algal cultivation system at the pilot scale was by the controlled addition of compressed stack gas. However, at full scale Amine Guard was the most cost-effective solution. The capital cost for an Amine Guard system to capture CO_2 from the Kellogg stack was estimated to be about 1.3 times higher than for a stack gas compression system but the operating costs of the stack gas compression system were about 2.5 times higher than the Amine Guard system. The high operating costs for direct stack gas compression are due primarily to the high energy requirement for cooling and compressing the larger volume of gas. The total life-cycle costs for the Amine Guard system to supply CO_2 for a full-scale algal cultivation system were therefore lower than the direct compression of stack gas.

In general, optimization of algal growth in the Hopewell caprolactam plant wastewater is challenging because (1) the nitrogen concentration in the wastewater fluctuates significantly (concentrations of 40mg/l to 120 mg/l of total dissolved nitrogen and 10 mg/l up to 80 mg/l of dissolved organic nitrogen were registered during the two months of experimental trials);and (2) the algae coexist with a bacteria culture that transforms the organic nitrogen into an inorganic form that is subsequently used for algae consumption. The best experimental results observed during the trial period showed a 30% nitrogen reduction after five days.

Bacterial activity is needed to convert organic nitrogen into ammonia-N. Experimental results show that this process takes days to complete. Such a process is more effectively done in deeper ponds than those required for high algae productivities, especially when land use is constrained. Therefore, a two-stage process may be

preferred when using algae to remediate industrial wastewater. Organic nitrogen would be converted into inorganic ammonia-N in a first stage and in a second stage algae would be cultivated to incorporate inorganic nitrogen into algae biomass.

Regulation of system carbon dioxide concentration is a common need in all algae systems where high algae growth rates are required. To obtain high growth rates, it is critical that dissolved CO_2 remains at a sufficiently high concentration. Since the rate of CO_2 consumption for optimal growth is highly variable during the diurnal cycle, being zero during night time and maximal during midday maximum sunlight hours, effective utilization of CO_2 can only be achieved by continuous online monitoring and control.

Traditional control systems for algae ponds include pH control using a mixture of air and CO_2 sparging. However, this study showed that such a strategy is not adequate to optimize algae growth in industrial wastewater due to the buffering capacity of the medium. The Honeywell team implemented an independent control strategy for dissolved CO_2 and pH. By controlling pH and dissolved CO_2 levels, the project was able to decouple the effects of pH and dissolved CO_2 on algae growth.

The Honeywell sensor and control system was shown to be capable of controlled addition of CO_2 to the Hopewell algal cultivation system. However, one of the results from the experimental trials was that CO_2 addition in the algae tanks was not needed in this particular setting. High concentrations of organic material in the wastewater led to significant bacterial activity which increased CO_2 levels above the limiting concentration for algae growth. CO_2 addition therefore provided no additional benefit for algae growth at the Hopewell site.

TABLE OF CONTENTS

REPORT DETAILS

1. EXPERIMENTAL METHODS

During Phase 1 of this project, the Hopewell team developed a detailed design for the Small Scale Pilot-Scale Algal CO_2 Sequestration System. This pilot consists of six (6) x 135 gallon cultivation tanks including the CO_2 delivery and control system, algal cultivation system and algal harvesting. A feed tank supplied Hopewell wastewater to the tanks and a receiver tank collected the effluent from the algal cultivation system.

1.1 SITE LOCATION AND LAYOUT

The location and design of the pilot at the Hopewell location is shown in Figures 1-4.

Figure 1. Location of Honeywell Hopewell Plant.

Honeywell Resins & Chemicals Site

UOP A Honeywell Company

Test Location and Physical Set-Up

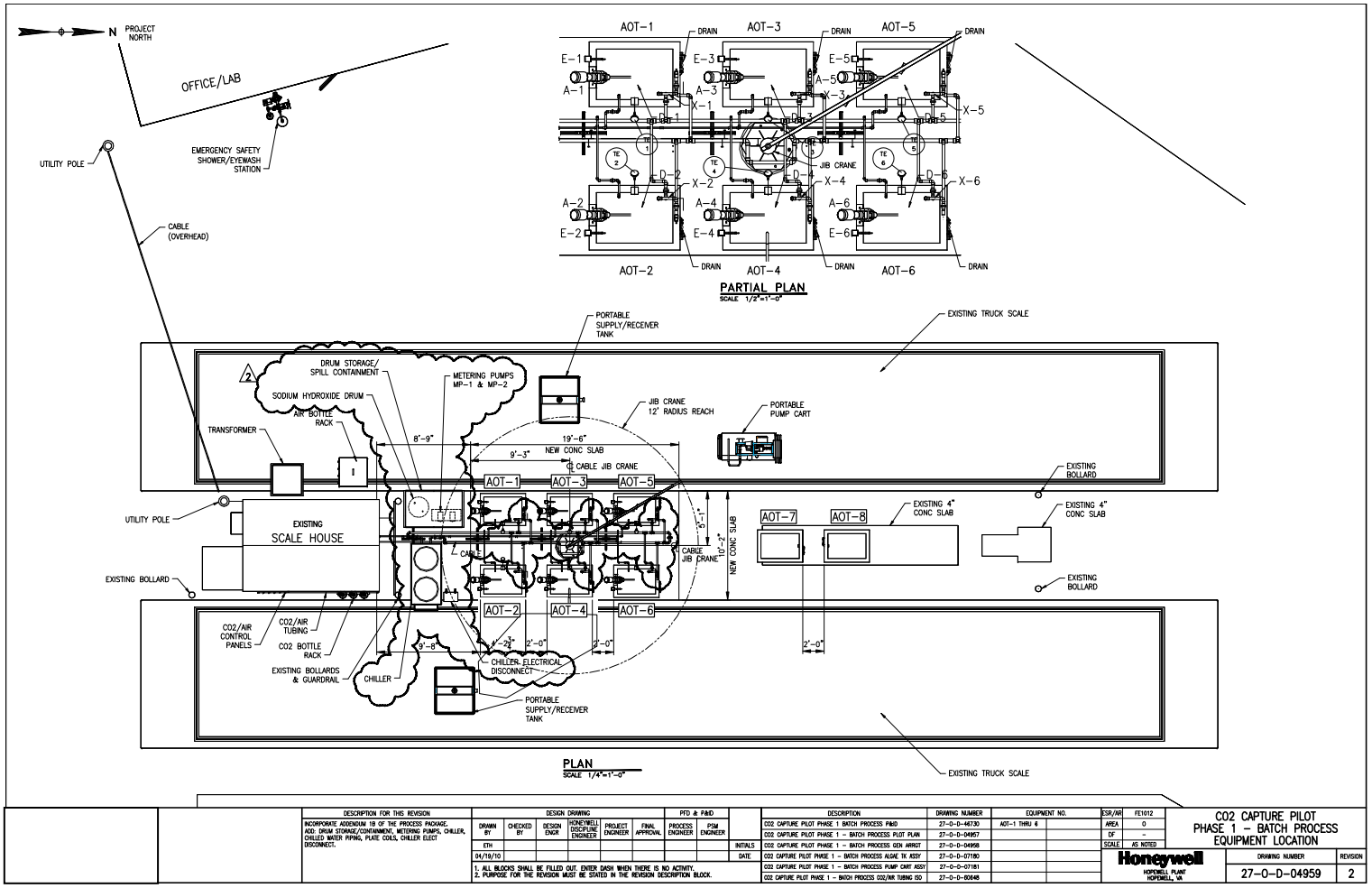
905 E. Randolph Rd, Hopewell, VA, 23860

Figure 1 (continued). Location of Honeywell Hopewell Plant.

Honeywell Resins & Chemicals Hopewell Plant

Test Site Contained Within Hopewell Site

Figure 2 – Layout of Algal Pilot Tanks on Site



DESCRIPTION FOR THIS REVISION	DESIGN DRAWING						PFD & P&ID			DESCRIPTION	DRAWING NUMBER	EQUIPMENT NO.	ESR/AR	FE1012	CO2 CAPTURE PILOT PHASE 1 – BATCH PROCESS EQUIPMENT LOCATION
INCORPORATE ADDENDUM 1B OF THE PROCESS PACKAGE. ADD: DRUM STORAGE/CONTAINMENT, METERING PUMPS, CHILLER, CHILLED WATER PIPING, PLATE COILS, CHILLER ELECT DISCONNECT.	DRAWN BY	CHECKED BY	DESIGN ENGR	HONEYWELL DISCIPLINE ENGINEER	PROJECT ENGINEER	FINAL APPROVAL	PROCESS ENGINEER	PSM ENGINEER		CO2 CAPTURE PILOT PHASE 1 BATCH PROCESS P&ID	27-0-D-44730	AOT-1 THRU 6	AREA	0	
	ETH								INITIALS	CO2 CAPTURE PILOT PHASE 1 – BATCH PROCESS PLOT PLAN	27-0-D-04957		DF	–	
	04/19/10								DATE	CO2 CAPTURE PILOT PHASE 1 – BATCH PROCESS GEN ARRGT	27-0-D-04958		SCALE	AS NOTED	
1. ALL BLOCKS SHALL BE FILLED OUT. ENTER DASH WHEN THERE IS NO ACTIVITY. 2. PURPOSE FOR THE REVISION MUST BE STATED IN THE REVISION DESCRIPTION BLOCK.										CO2 CAPTURE PILOT PHASE 1 – BATCH PROCESS ALGAE TK ASSY	27-0-D-07180		Honeywell		DRAWING NUMBER / REVISION
										CO2 CAPTURE PILOT PHASE 1 – BATCH PROCESS PUMP CART ASSY	27-0-D-07181		HOPEWELL PLANT HOPEWELL, VA		27-0-D-04959 / 2
										CO2 CAPTURE PILOT PHASE 1 – BATCH PROCESS CO2/AIR TUBING ISO	27-0-D-80048				

Figure 3 – Hopewell Phase 1 Small Scale Algal CO_2 Re-Use Pilot Design

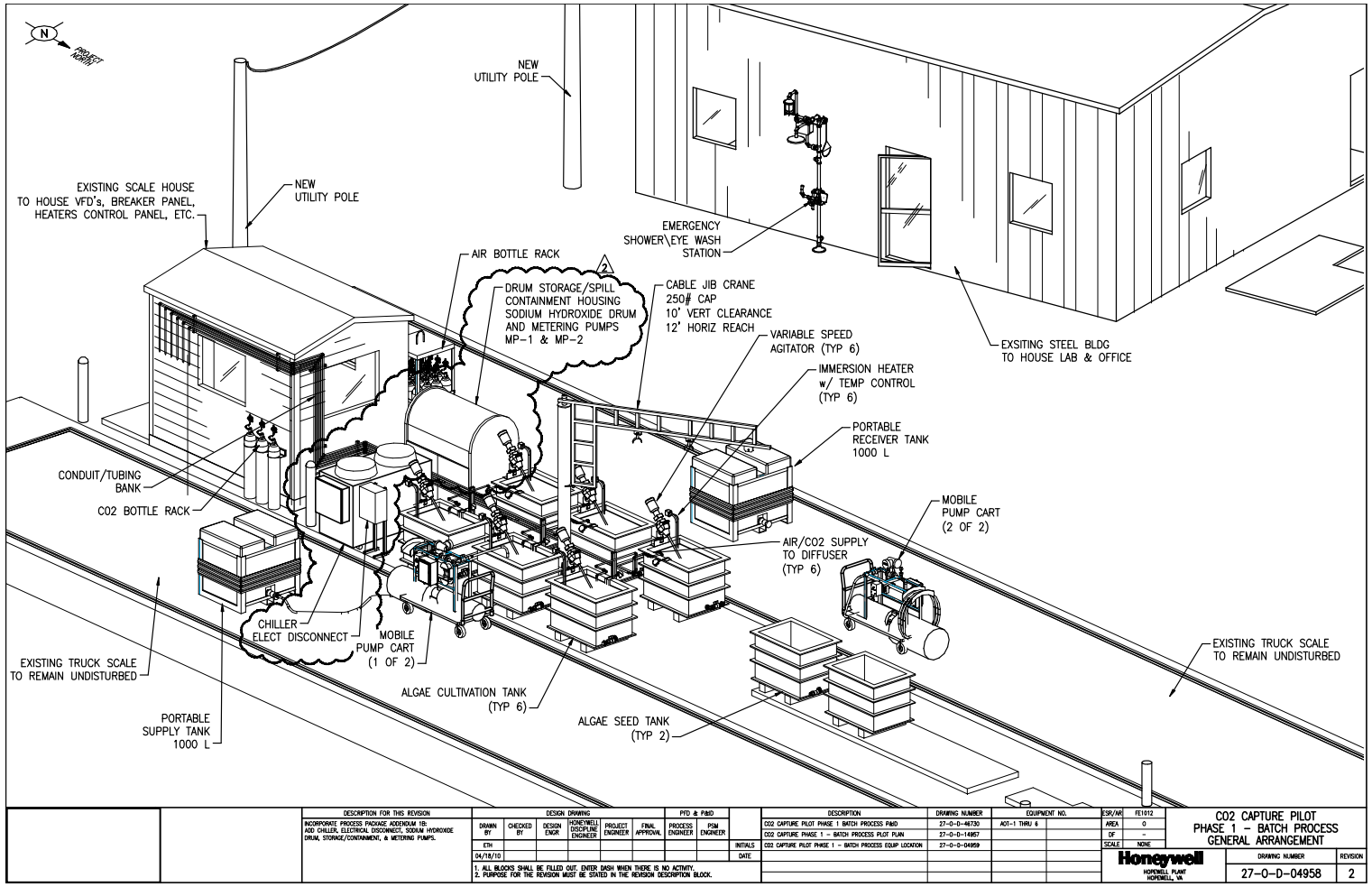
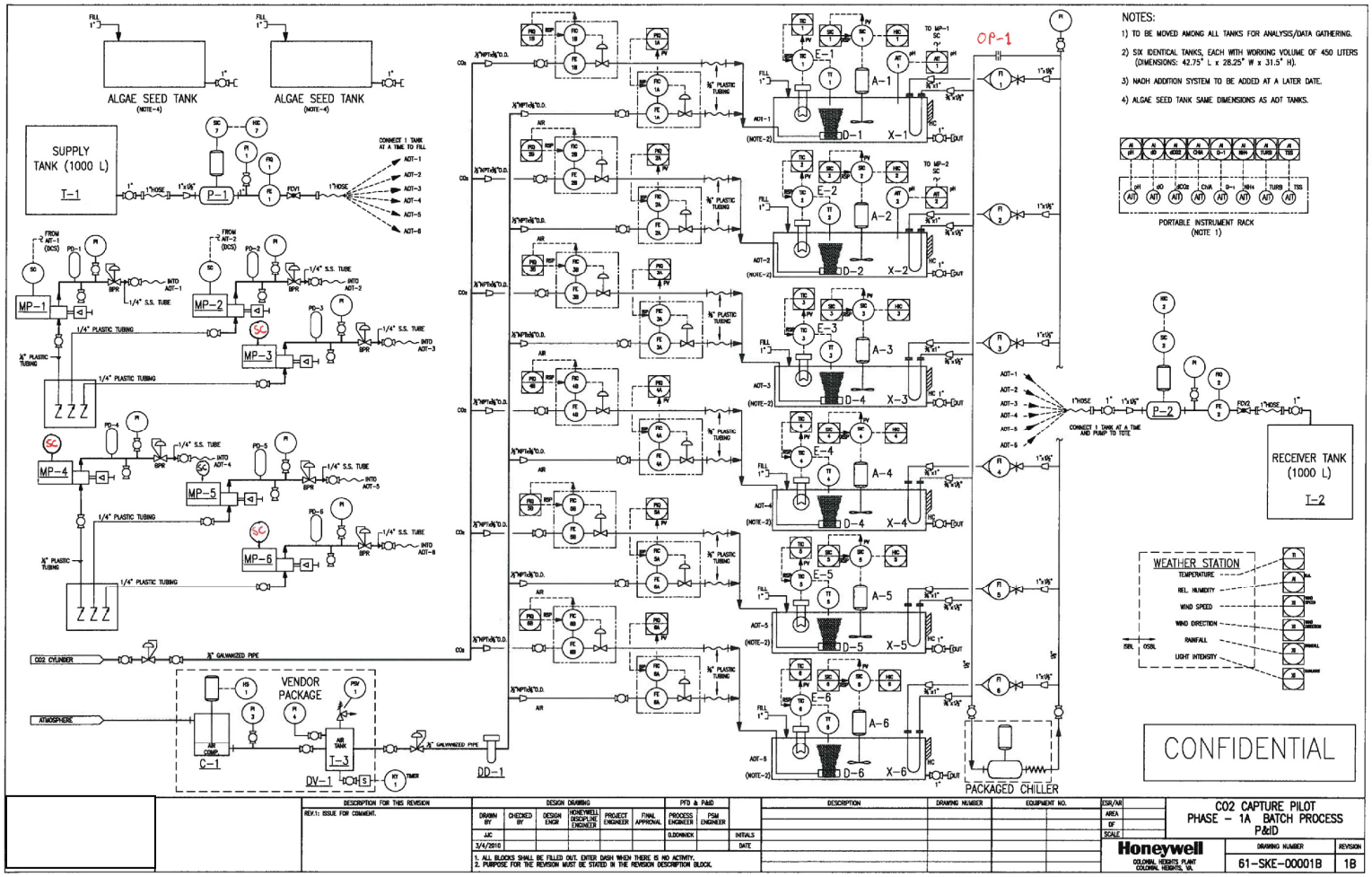


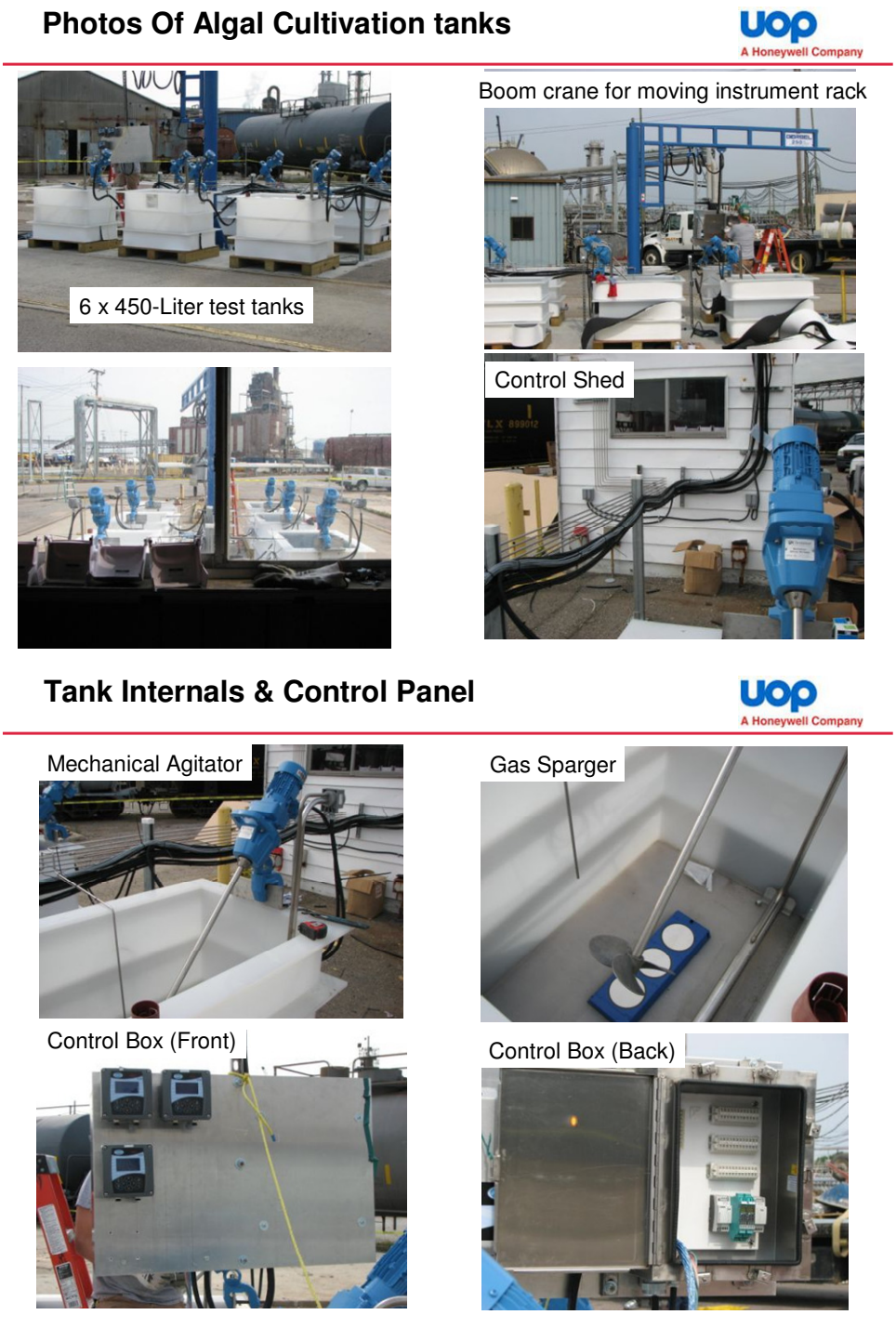
Figure 4 – Hopewell Phase 1 Small Scale Algal CO_2 Re-Use Pilot Schematic



1.2 ALGAL CULTIVATION SYSTEM AND CONTROLS

The constructed tanks are shown in Figure 5:

Figure 5 – Algal Cultivation Tanks



Each of the six cultivation units was operated under differing environmental conditions, nutrient regimes or CO_2 control strategies to enable a direct and side by side comparison of the impacts of these variables upon the rate of algal growth, CO_2 uptake and conversion to algal biomass and bio-fuel precursors.

The algal inoculums for the tests were obtained from enrichments of James River water samples obtained immediately adjacent to the plant. These initial enrichments were used for further enrichments at UOP's lab facilities in Des Plaines, IL into samples of wastewater obtained from the wastewater retention ponds at the Hopewell plant. Thus the algae used in these trials are locally obtained species that are native to the Hopewell location and are able to proliferate in the wastewater matrix generated at the Hopewell site.

The algal cultures were transferred from Des Plaines to be mixed in with cultures already growing in the algal seed tanks at Hopewell. Two tanks of about 130 gallons in capacity were used to prepare inoculums of about 30% into the trial tanks at the start of the operational phase. Once the algae in the trial tanks were mature, fresh Hopewell wastewater was added to the cultivation tanks and the test phase commenced.

Naturally occurring algae from the James River were found to grow very quickly on the Hopewell wastewater once this water was amended with phosphorous nutrients. The wastewater has a relatively high concentration of nitrogen contaminants that are conducive to algal growth. This was observed in the starter enrichments in UOP's Des Plaines Lab as well as in the field at Hopewell.

Pictures of the algal seed tanks are shown in Figure 6.

Figure 6 – Algal Seed Tanks at the Hopewell Site

During the test phase, the Honeywell Process Control system measured key critical parameters such as temperature, pH, ammonia, chlorophyll density, turbidity, dissolved oxygen and dissolved CO_2. The resulting data were used and analyzed to institute automated DCS control of addition of CO_2 and caustic to control pH and to maintain and optimal soluble CO_2 concentration for growth in some of the trial tanks.

The performance of these tanks versus tanks without the automated control were evaluated. Also, the effects of key critical parameters such as temperature and nutrient loading on these controlled and uncontrolled tanks were evaluated. The test led to the development of an effective, automated system for the monitoring and control of CO_2 addition.

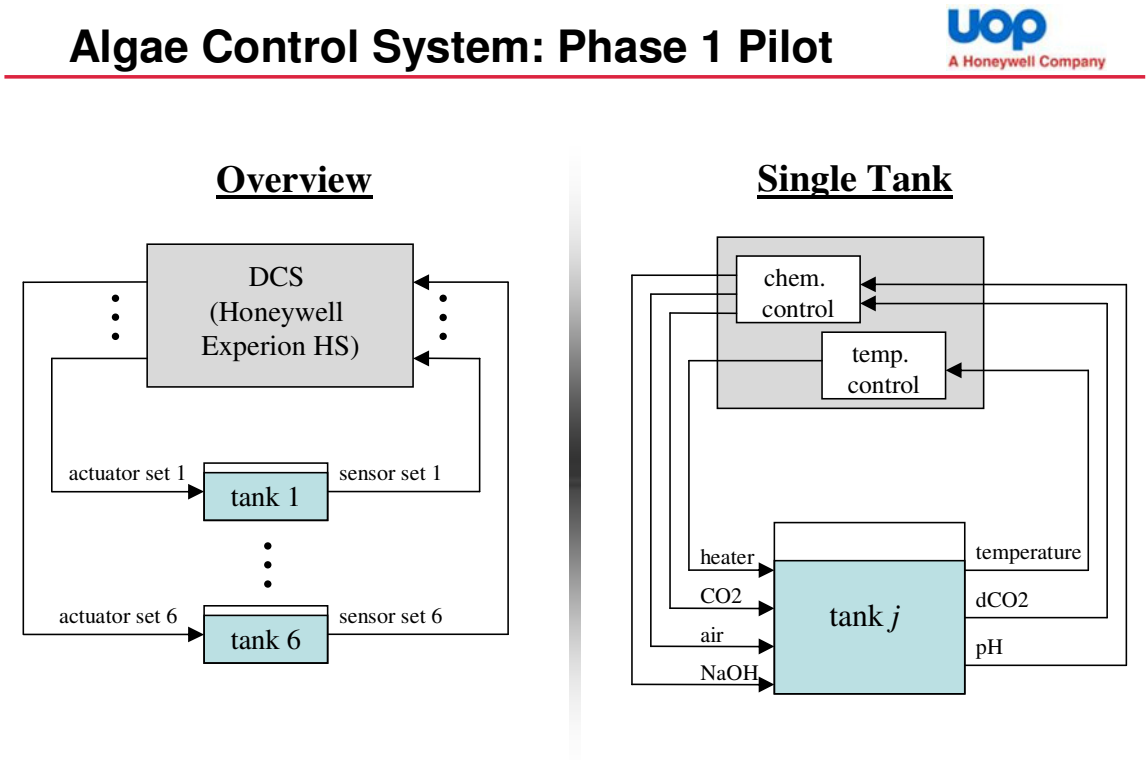
The cultivation of algae in the Hopewell Pilot tanks is shown in Figures 7 and 8.

Figure 7. Example of Algal Growth Tank.

Figure 8. Example of Fully-Instrumented Algae Tank.

Figure 9 outlines the control scheme for the algal pilot.

Figure 9 – Control Scheme for Algal Cultivation



The effect of the chemistry and nutrient loading of the Hopewell wastewater on algal cultivation was assessed by an extensive analytical test regime. These analyses included measurement of:

- pH
- Temperature,
- Ammonia
- Total Nitrogen and Total Dissolved Nitrogen
- Total Phosphorous and Total Dissolved Phosphorous
- Chemical Oxygen Demand (COD)
- Total Suspended Solids (TSS)
- Turbidity
- Chlorophyll A
- Dissolved Oxygen (DO) and Dissolved CO_2
- Conductivity

1.3 EXPERIMENT DESIGN

The strategy for determining the critical growth parameters is shown in Figure 10.

Figure 10 – Determination of Critical Parameters for Algal Growth at Hopewell

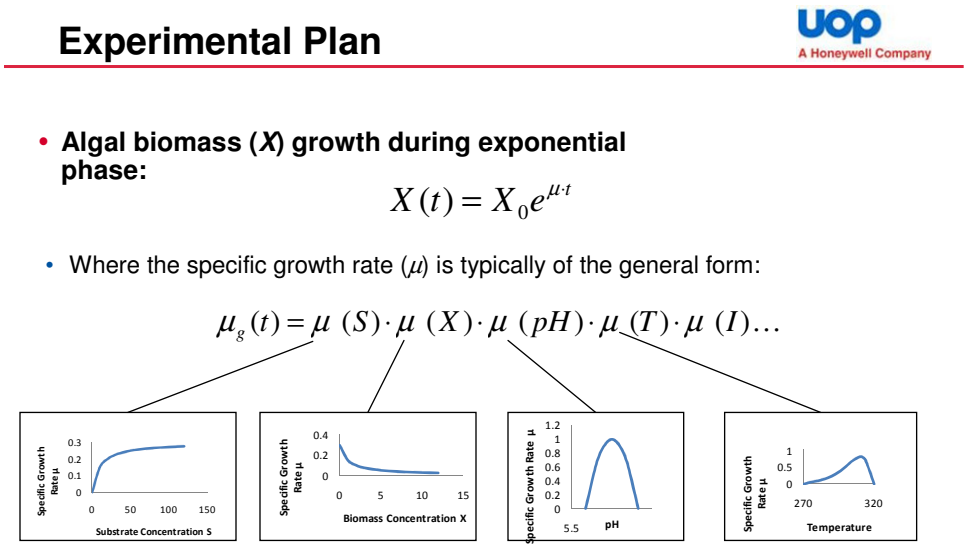
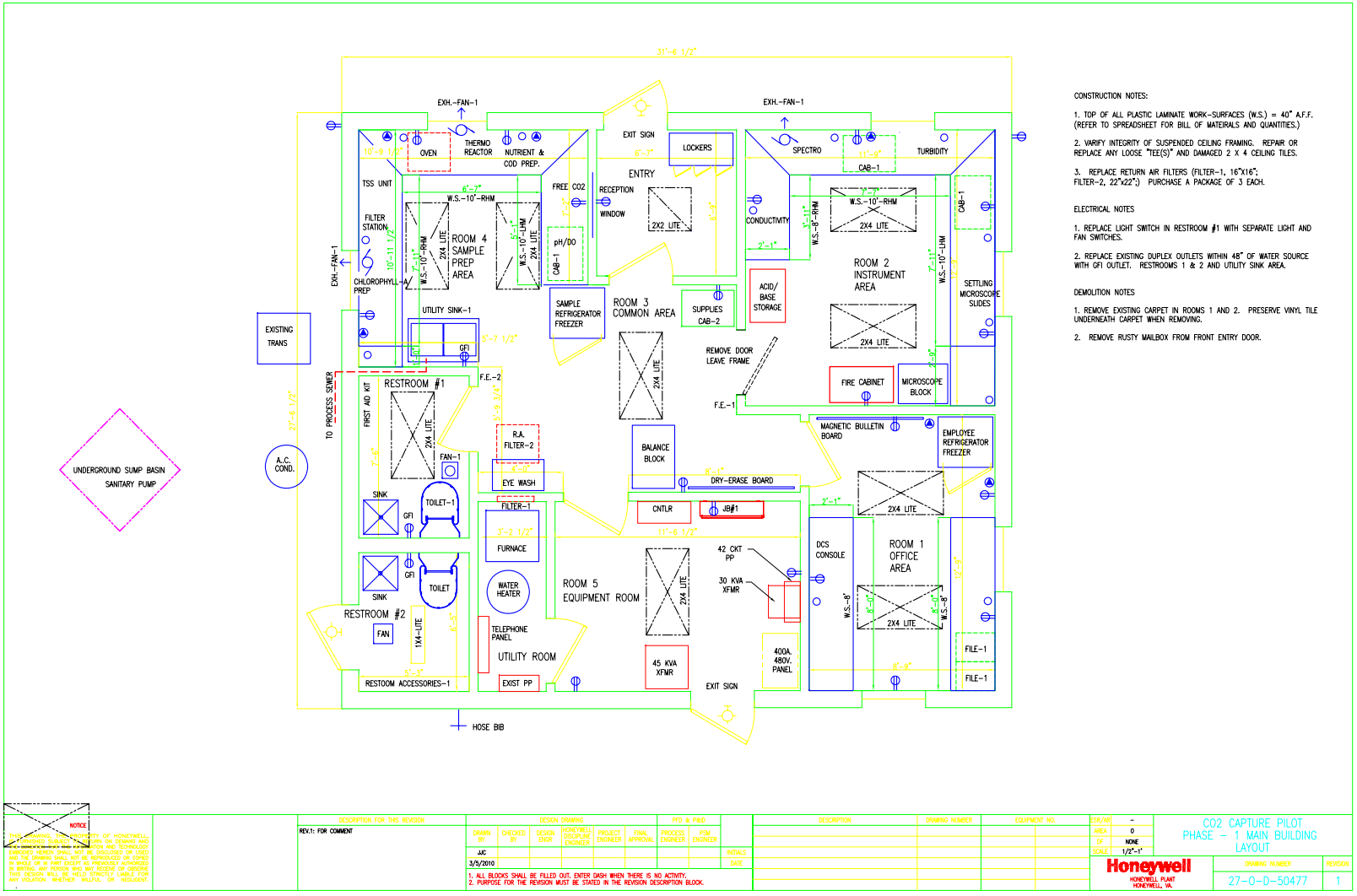


Table 1 – Experimental Design Overview

Week	Experiment
1, 3, 5	Evaluate effect of N:P ratio and CO_2 addition.
2, 4, 6	Evaluate effect of temperature, pH and air flow.
7	Evaluate effect of dissolved CO_2 concentration, air flow and temperature.
8	Evaluate effect of dissolved CO_2 concentration, excess micronutrients and high seed concentration.
9,10	Evaluate effect of dissolved CO_2 concentration.
11	Evaluate effect of dissolved CO_2 concentration and gas addition.
12	Evaluate effect of dissolved CO_2 concentration, gas addition, high seed concentration and water medium.

A support lab was established to conduct on-site testing during Phase 1 as shown in Figure 11.

Figure 11 – Support Facilities for Phase 1 and Phase 2



CONSTRUCTION NOTES:

1. TOP OF ALL PLASTIC LAMINATE WORK-SURFACES (W.S.) = 40" A.F.F. (REFER TO SPREADSHEET FOR BILL OF MATEIRALS AND QUANTITIES.)

2. VARIFY INTEGRITY OF SUSPENDED CEILING FRAMING. REPAIR OR REPLACE ANY LOOSE "TEE(S)" AND DAMAGED 2 X 4 CEILING TILES.

3. REPLACE RETURN AIR FILTERS (FILTER-1, 16"X16", FILTER-2, 22"x22".) PURCHASE A PACKAGE OF 3 EACH.

ELECTRICAL NOTES

1. REPLACE LIGHT SWITCH IN RESTROOM #1 WITH SEPARATE LIGHT AND FAN SWITCHES.

2. REPLACE EXISTING DUPLEX OUTLETS WITHIN 48" OF WATER SOURCE WITH GFI OUTLET. RESTROOMS 1 & 2 AND UTILITY SINK AREA.

DEMOLITION NOTES

1. REMOVE EXISTING CARPET IN ROOMS 1 AND 2. PRESERVE VINYL TILE UNDERNEATH CARPET WHEN REMOVING.

2. REMOVE RUSTY MAILBOX FROM FRONT ENTRY DOOR.

NOTICE
THIS DRAWING IS THE PROPERTY OF HONEYWELL AND IS LOANED SUBJECT TO RETURN ON DEMAND AND WITH THE UNDERSTANDING THAT THE INFORMATION AND TECHNOLOGY EMBODIED HEREIN SHALL NOT BE DISCLOSED OR USED AND THIS DRAWING SHALL NOT BE REPRODUCED OR COPIED IN WHOLE OR IN PART EXCEPT AS PREVIOUSLY AUTHORIZED IN WRITING. ANY PERSON WHO ANY ROOTS OF DISCLOSE THIS DESIGN WILL BE HELD STRICTLY LIABLE FOR ANY VIOLATION WHETHER WILFUL OR INVOLUNTARY.

DESCRIPTION FOR THIS REVISION: REV.1: FOR COMMENT

DESIGN DRAWING	DRAWN BY	CHECKED BY	DESIGN ENGR.	HONEYWELL DESIGN AGENT ENGINEER	PROJECT ENGINEER	FINAL APPROVAL	PFD & P&ID: PROCESS ENGINEER	PSM ENGINEER	INITIALS
	JJC								DATE
	3/5/2010								

1. ALL BLOCKS SHALL BE FILLED OUT. ENTER DASH WHEN THERE IS NO ACTIVITY.
2. PURPOSE FOR THE REVISION MUST BE STATED IN THE REVISION DESCRIPTION BLOCK.

DESCRIPTION	DRAWING NUMBER	EQUIPMENT NO.

CSR/AR	-
AREA	0
DF	NONE
SCALE	1/2"=1'

CO2 CAPTURE PILOT
PHASE - 1 MAIN BUILDING LAYOUT

Honeywell
HONEYWELL PLANT
HONEYWELL, VA.

DRAWING NUMBER	REVISION
27-0-D-50477	1

The algal biomass produced during the test was flocculated and settled in the receiving at certain intervals to collect enough algal biomass for shipment to Des Plaines for evaluation of conversion to fuels using novel oil extraction and processing processes.

An important feature of the Hopewell Phase 1 testing was to evaluate the accuracy and reliability of online sensors against conventional wet chemical analyses. In addition, the accuracy of on-site wet chemical analyses was compared to duplicate analyses conducted by an off-site certified environmental laboratory.

A comprehensive set of experimental trials was performed during the months of May, June and July 2010 to determine the feasibility and scale-up requirements for an algae farm at the Honeywell Hopewell caprolactam plant. The goal of the experiments was to determine the rate of nitrogen reduction, algae and non-algae biomass growth rate and the conversion rate of CO_2 into algal biomass. Experimental trials were also aimed at determining critical process variables that need to be monitored in-situ for control. Experiments were performed in batch tanks and were monitored over a 5 day period. A total of six tanks were used for the experiments. Samples were collected every day to analyze algal and total biomass concentrations and chemical composition of the water medium (Figure 12). Samples were analyzed internally and externally by a subcontracted laboratory to validate the measurements. Online sensor measurements were also available to compare with the internal lab results. With three sets of data, cross correlation was possible to confirm the overall validity of the data acquired. Only internal laboratory measurements are used in the data analysis.

Figure 12 – Measurement of Nutrients in Hopewell Wastewater with HACH Spectrometer

The Detailed Experimental Design is for Phase 1 is shown in Tables 2 and 3.

Table 2 – Experimental Design Parameters

	Levels			
Parameters	**Nominal**	**Ambient**	**High**	**Low**
N:P Ratio	10:1	Unmodified Hopewell effluent	30:1	3:1
Dissolved CO2 concentration	No feedback control (or manual adjustments) of CO2 flow to keep a constant dCO2 concentration.	No CO2 sparging	95 (via CO2 addition)	20 (via CO2 addition)
pH set-point	7 (via CO2 addition)	As in Hopewell effluent	8.5 (via CO2 addition)	6 (via CO2 addition)
Light Intensity	-	Normal daylight intensity	-	-
Mixing Speed	150 RPM	-	-	-

Table 3. Matrix of Trials by Week

Week	Tank #1		Tank #2		Tank #3		Tank #4		Tank #5		Tank #6		Notes
1	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Evaluate effect of N:P ratio and no CO2 addition.
	N:P Ratio	**Low**	N:P Ratio	**Ambient**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**High**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	
	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Ambient**	pH set-point	**Nominal**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**No**	
	Experiment #	**1-1**	Experiment #	**1-2**	Experiment #	**1-3**	Experiment #	**1-4**	Experiment #	**1-5**	Experiment #	**1-6**	
2	Temperature	**30**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Evaluate effect of temperature, pH and air. ** with high air flow rate
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	
	pH set-point	**Nominal**	pH set-point	**High**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Low**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	
	Experiment #	**2-1**	Experiment #	**2-2**	Experiment #	**2-3****	Experiment #	**2-4**	Experiment #	**2-5**	Experiment #	**2-6**	

Week	Tank #1		Tank #2		Tank #3		Tank #4		Tank #5		Tank #6		Notes
3	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Evaluate effect of N:P ratio and no CO2 addition. (**Repeat Week 1**)
	N:P Ratio	**Low**	N:P Ratio	**Nominal**	N:P Ratio	**High**	N:P Ratio	**Ambient**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	
	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	dCO2 concentration	**Ambient**	
	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Ambient**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**No**	Seeded	**Yes**	Seeded	**Yes**	
	Experiment #	**3-1**	Experiment #	**3-2**	Experiment #	**3-3**	Experiment #	**3-4**	Experiment #	**3-5**	Experiment #	**3-6**	
4	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**30**	Temperature	**20**	Evaluate effect of temperature, pH and air. (**Repeat Week 2**) ** with high air flow rate
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	
	pH set-point	**Low**	pH set-point	**High**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	
	Experiment #	**4-1**	Experiment #	**4-2**	Experiment #	**4-3****	Experiment #	**4-4**	Experiment #	**4-5**	Experiment #	**4-6**	

Week	Tank #1		Tank #2		Tank #3		Tank #4		Tank #5		Tank #6		Notes
5	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Evaluate effect of N:P ratio and no CO2 addition. (**Repeat Week 1**)
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**High**	N:P Ratio	**Low**	N:P Ratio	**Ambient**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	
	pH set-point	**Nominal**	pH set-point	**Ambient**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**No**	
	Experiment #	**5-1**	Experiment #	**5-2**	Experiment #	**5-3**	Experiment #	**5-4**	Experiment #	**5-5**	Experiment #	**5-6**	
6	Temperature	**20**	Temperature	**20**	Temperature	**10**	Temperature	**30**	Temperature	**20**	Temperature	**20**	Evaluate effect of temperature, and pH (**Repeat Week 2**)
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	
	pH set-point	**Low**	pH set-point	**High**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	
	Experiment #	**6-1**	Experiment #	**6-2**	Experiment #	**6-3**	Experiment #	**6-4**	Experiment #	**6-5**	Experiment #	**6-6**	

Week	Tank #1		Tank #2		Tank #3		Tank #4		Tank #5		Tank #6		Notes
7	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**10**	Temperature	**20**	Evaluate effect of dCO2 concentration, air flow and temperature. * pH adjusted via NaOH addition ** with high air flow rate
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Low**	dCO2 concentration	**High**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	
	pH set-point	**Nominal***	pH set-point	**Nominal***	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	
	Experiment #	**7-1**	Experiment #	**7-2**	Experiment #	**7-3**	Experiment #	**7-3****	Experiment #	**7-5**	Experiment #	**7-6**	
8	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Evaluate effect of dCO2 concentration and initial seed concentration. * pH adjusted via NaOH addition ***with excess micronutrients
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Low**	dCO2 concentration	**High**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	
	pH set-point	**Nominal***	pH set-point	**Nominal***	pH set-point	**Nominal**	pH set-point	**Ambient**	pH set-point	**Nominal**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes (high seed concentration)**	
	Experiment #	**8-1**	Experiment #	**8-2**	Experiment #	**8-3**	Experiment #	**8-4**	Experiment #	**8-5*****	Experiment #	**8-6**	

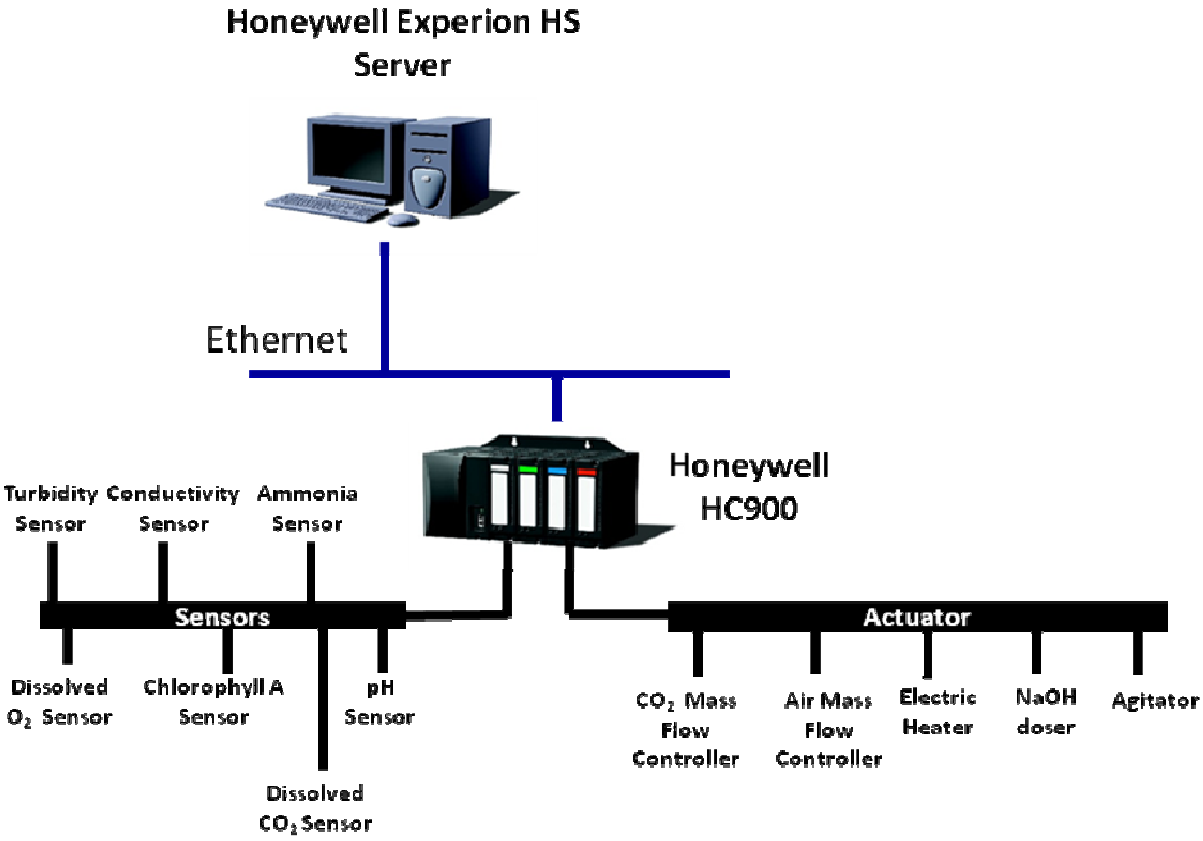
Week	Tank #1		Tank #2		Tank #3		Tank #4		Tank #5		Tank #6		Notes
9	Temperature	**25**	Temperature	**25**	Temperature	**25**	Temperature	**25**	Temperature	**25**	Temperature	**25**	Evaluate effect of dCO2 concentration and temperature (fine grid). * pH adjusted via NaOH addition
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Low**	dCO2 concentration	**High**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	dCO2 concentration	**Ambient**	
	pH set-point	**Nominal***	pH set-point	**Nominal***	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Ambient**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	
	Experiment #	**9-1**	Experiment #	**9-2**	Experiment #	**9-3**	Experiment #	**9-4**	Experiment #	**9-5**	Experiment #	**9-6**	
10	Temperature	**25**	Temperature	**25**	Temperature	**25**	Temperature	**25**	Temperature	**25**	Temperature	**25**	Evaluate effect of dCO2 concentration and temperature (fine grid). * pH adjusted via NaOH addition (**Repeat Week 9**)
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Low**	dCO2 concentration	**High**	dCO2 concentration	**Nominal**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	dCO2 concentration	**Ambient**	
	pH set-point	**Nominal***	pH set-point	**Nominal***	pH set-point	**Nominal**	pH set-point	**Nominal**	pH set-point	**Ambient**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	
	Experiment #	**10-1**	Experiment #	**10-2**	Experiment #	**10-3**	Experiment #	**10-4**	Experiment #	**10-5**	Experiment #	**10-6**	

Week	Tank #1		Tank #2		Tank #3		Tank #4		Tank #5		Tank #6		Notes
11	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Evaluate effect of dCO2 concentration and gas addition . * pH adjusted via NaOH addition
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	N:P Ratio	**Ambient**	
	dCO2 concentration	**Low**	dCO2 concentration	**High**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	dCO2 concentration	**Ambient**	dCO2 concentration	**Ambient**	
	pH set-point	**Nominal***	pH set-point	**Nominal***	pH set-point	**Nominal**	pH set-point	**Ambient**	pH set-point	**Ambient**	pH set-point	**Ambient**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	
	Experiment #	**11-1**	Experiment #	**11-2**	Experiment #	**11-3**	Experiment #	**11-4**	Experiment #	**11-5**	Experiment #	**11-6**	
12	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Temperature	**20**	Evaluate effect of dCO2 concentration, gas addition, initial seed concentration and water medium. * pH adjusted via NaOH addition
	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Nominal**	N:P Ratio	**Ambient**	N:P Ratio	**Nominal**	
	dCO2 concentration	**Low**	dCO2 concentration	**High**	dCO2 concentration	**Nominal**	dCO2 concentration	**Ambient**	dCO2 concentration	**Ambient**	dCO2 concentration	**Nominal**	
	pH set-point	**Nominal***	pH set-point	**Nominal***	pH set-point	**Nominal**	pH set-point	**Ambient**	pH set-point	**Ambient**	pH set-point	**Nominal**	
	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	Light Intensity	**Ambient**	
	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	Mixing Speed	**Nominal**	
	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes**	Seeded	**Yes (high seed concentration)**	Seeded	**Yes (potable water instead of wastewater)**	
	Experiment #	**12-1**	Experiment #	**12-2**	Experiment #	**12-3**	Experiment #	**12-4**	Experiment #	**12-5**	Experiment #	**12-6**	

1.4 SENSORS AND CONTROL SYSTEM

A Honeywell control system was commissioned for data acquisition and control of the algae batch tanks. The control system consisted of a Honeywell HC900 Hybrid Controller connected via Ethernet to a Honeywell Experion HS server for visualization and storage of process data. A schematic drawing of the control system is shown in Figure 13.

Figure 13 Schematic drawing of control system



The Honeywell HC900 Controller is an integrated loop and logic controller designed specifically for small- and medium-scale unit operations. It comprises a set of hardware and software modules that can be assembled to satisfy any broad range of process control applications. The HC900 Controller can consist of a single rack, as indicated in Figure 13, or can be networked with other controllers via Ethernet links to expand the dimensions of control over a wider range of unit processes. The HC900 Controller includes provisions for communication via Ethernet with host systems that supports Ethernet Modbus/TCP protocol.

The batch tanks were equipped with a suite of control instrumentation. The Honeywell HC 900 was used to connect via 4-20 mA signals to a set of sensors mounted on a portable rack on top of the experimental tanks. The sensors were used to measure turbidity, Chlorophyll A, dissolved oxygen, pH, ammonia, and conductivity every day for approximately two hours per tank. The HC900 was also connected to the final control elements such as air and CO_2 flow controllers, agitator speed controllers, electric heaters

and NaOH dosing pumps. Connections were also provided to hook the HC900 to a set of fixed sensors on two of the experimental tanks to measure pH and dissolved CO_2.

Table 4 summarizes the sensors used in the experiments and Table 5 shows the instrumentation available in each experimental tank. All inputs and outputs from the tank's sensors and actuators were stored historically in the Honeywell Experion server for data analysis. To maximize sensing capabilities, while keeping the sensors' expenses within budget, only two tanks were equipped with the required instrumentation for automatic pH and dissolved CO_2 control (Figure 14).

Table 4 – Sensors for Measurement of Key Process Parameters

Measurement	Purpose
pH	pH is critical to algal growth (6 – 8)
Temperature	Temp is critical to algal growth (10-40°C)
Dissolved CO_2	Main determining factor in growth. Expensive to deliver
Dissolved O_2	Need at night by Algae. Needed to control anaerobic bacteria. Anaerobic bacteria breaks down organic N.
Ammonium	Main nutrient for algal growth.
Chlorophyll, Turbidity	Indirect measurement of algal growth
Conductivity	Characterize the salinity of the medium – algal growth can be dependent upon this

Table 5 – Instrumentation set-up for each experimental tank

TANK #	Air Flow Control	CO2 Flow Control	Mixing Control	Temperature Control	Automatic pH Control	Automatic dissolved CO2 Control
1	Yes	Yes	Yes	Yes	Yes	Yes
2	Yes	Yes	Yes	Yes	Yes	Yes
3	Yes	Yes	Yes	Yes	No	No
4	Yes	Yes	Yes	Yes	No	No
5	Yes	Yes	Yes	Yes	No	No
6	Yes	Yes	Yes	Yes	No	No

Figure 14 – Instrumentation on Tank 1

2. RESULTS AND DISCUSSION

2.1 COMPARISON OF CARBON DIOXIDE CAPTURE AND DELIVERY SYSTEMS

During Phase 1, the UOP Gas Processing group evaluated two scenarios for the supply of CO_2 to the algal pilot. The first scenario involved the direct compression and delivery of straight flue gas to the algal cultivation system. The second scenario involved the use of an Amine Guard Flue Gas CO_2 capture system to capture and supply a pure stream of CO_2 to the algal cultivation ponds. The concentration of carbon dioxide in the Kellogg Stack at Hopewell is approximately 7%. In both cases CO_2 was delivered to the plant via sparging (Figure 15).

It was not immediately obvious which of these two approaches might be the most cost effective mechanism to provide the CO_2 required for enhanced algal growth. The amine unit can supply a pure, concentrated stream of CO_2 which would greatly reduce the volume of gas required and the associated piping from the Kellogg stack to the algal ponds. On the other hand, the amine unit cannot be switched on and off as the demand for CO_2 by the algal system changes with the diurnal periodicity. The only option is to either vent back the CO_2 back to the stack or find another outlet for the captured CO_2 besides the algal cultivation system.

UOP estimated the cost for both the direct stack compression and Amine Guard scenarios for both a Phase 2 pilot demonstration scale and a projected full-scale Hopewell CO_2 capture system. Also, UOP conducted an preliminary LCA on the stack-gas compression and amine CO_2 capture scenarios at full-scale at the Hopewell site.

UOP estimated both equipment costs and estimated erected cost (EEC) for both options. The direct field costs for the equipment items were based on Preliminary Equipment Data information provided in April 2010. These costs represent U.S. Gulf Coast erection to UOP standards for new equipment on a January 2010, open shop (non-union) labor basis. The equipment costs have an anticipated accuracy of +40% / -25%. The EEC is a factored cost, which includes installation, associated bulk items (such as instruments, electrical, piping, and civil), construction indirects, and contractor's home office expenses. The EEC has an anticipated accuracy of +50% / -30%. The EEC was for battery limits only. Construction indirect costs and home office expenses included in the EEC were not based on single equipment item installations; these equipment items are assumed to be part of a larger / typical refinery project. The cost of both the direct stack gas recovery and injection system and the Amine Guard CO_2 capture systems were estimated be greater than $1M even at the demonstration scale.

The cost of the Amine Guard system at demonstration scale was approximately 5 times more expensive than the direct stack gas injection system but this was based upon the fact that the Amine Guard unit was considerably oversized because the smallest commercially available pilot Amine Guard units had a much higher capacity than was required for demonstration scale.

A full scale, the Amine Guard unit capital costs were only 1.26 times more than the direct stack gas injection system. Conversely, the volume of pure CO_2 gas supplied by the Amine Guard system was 10 fold lower than that delivered by the direct stack gas

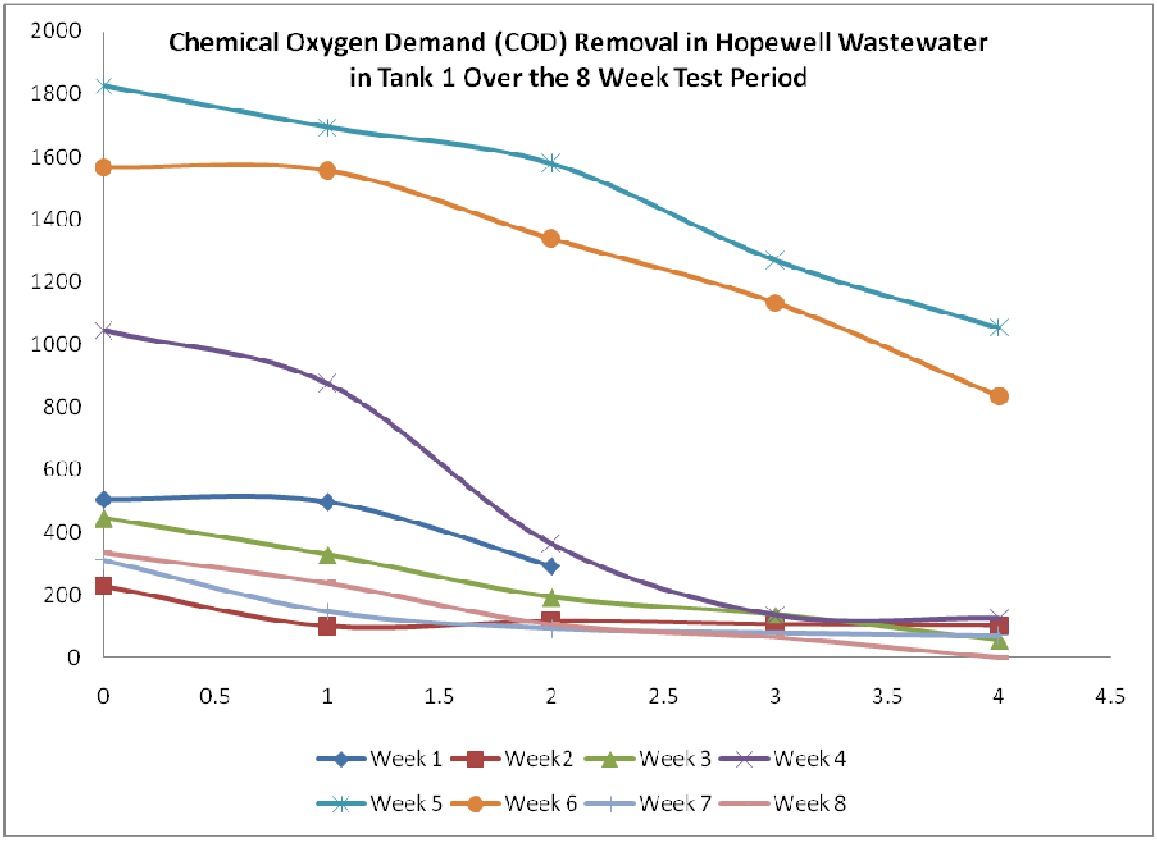
injection system. The utilities for the operation of the Amine Guard system were 1/3 that required for the direct stack gas compression system. The high utility requirement for the direct stack gas compression system was primarily due to the high electrical power usage for the stack gas compressors and the cooling requirement for the heat exchangers. These costs more than out weighed the cost for chemicals and adsorbent regeneration costs associated with Amine Guard system.

Figure 15 – CO_2 Sparging of Algal Pilot

2.2 ALGAL PRODUCTIVITY AND CO_2 UPTAKE

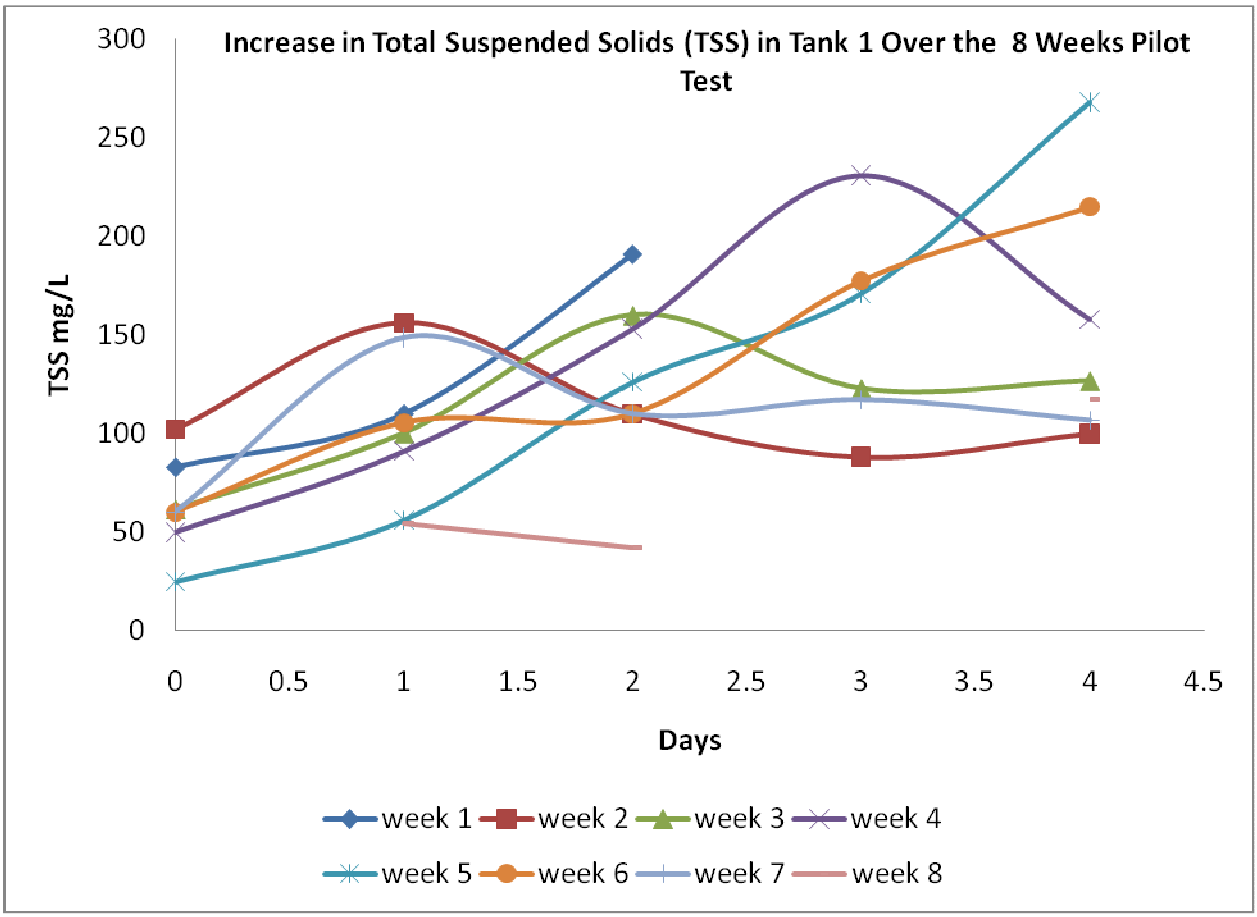
Initially it was expected that the pilot would demonstrate a high level of CO_2 uptake in the Hopewell wastewater due to the relatively warm temperature and high nitrogen content of the wastewater. It was expected that we would observe algal productivity in the order of 24 to a maximum of 65 g/m^2/day and CO_2 capture in excess of 40 g/m^2/day. The data from the pilot plant indicated that there was a significant amount of biomass growth in the wastewater but that this growth was actually a combination of bacterial growth and algal growth. The bacterial growth was promoted by the high amount of dissolved organic material present in the Hopewell Wastewater. Chemical Oxygen Demand (COD) is a measure of the amount of oxidizable organic material present in the wastewater. The variability of COD in the wastewater and the removal of COD during cultivation in Tank 1 is shown in Figure 16.

Figure 16 – Chemical Oxygen Demand Removal in Hopewell Pilot – Tank 1



The COD in the Hopewell wastewater ranged from 200 mg/L to up to 1800 mg/L. This organic material consisted of organic nitrogen species such as caprolactam and is a rich source of nutrients for heterotrophic bacterial growth. The metabolism of the heterotrophic bacteria resulted in the in-situ production of both CO_2 and ammonia which should have promoted algal growth but may also promote formation of non-algal biomass, competing with algal biomass for other essential nutrients such as phosphorous. The total biomass production in Tank 1 associated with both the algal and non-algal biomass is shown in the following figure:

Figure 17 – Total Suspended solids formation in Hopewell Pilot – Tank 1



Chlorophyll A measurement can be used to distinguish algal growth from non-algal biomass. The following formula was utilized to calculate the algal productivity in the Hopewell Pilot:

$$Algal\ Productivity = Algal\ TSS\ rate\ of\ production\ x\ Volume\ x\ \left(\frac{1}{Area}\right) x24$$

$$Algal\ TSS\ rate\ of\ production = Measured\ Chlorophyll\ rate\ of\ production\ \left(\frac{mg}{m3}\right) x\left(\frac{1}{1000}\right) x67$$

$$Area = 0.779\ m2$$

$$Volume = 450\ l$$

Figure 18 demonstrates the increase in chlorophyll as measured by the online Chlorophyll A sensor over a 3.5 day dinural cycle.

Figure 18 – Chlorophyll A Measurement in Hopewell Algal Cultivation Tank

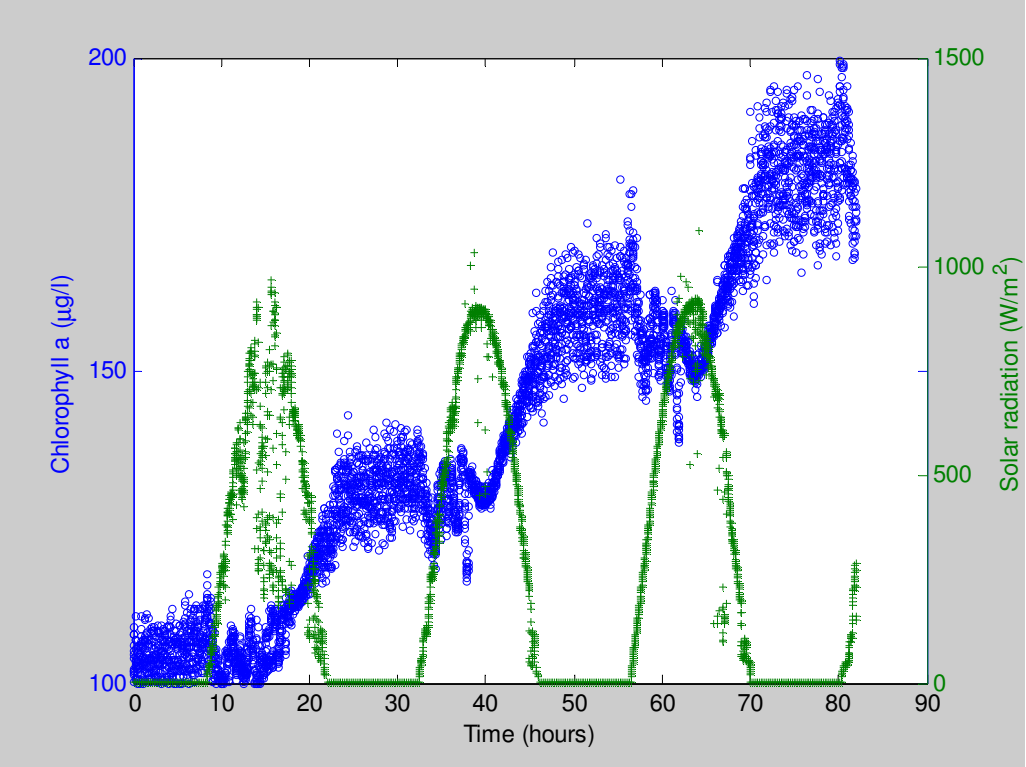


Table 6 shows the following rates of algal productivity were calculated for the Hopewell wastewater, using the total suspended solids and chlorophyll data and results from all six tanks under variable environmental conditions.

Table 6 – Algal Productivity

	Min	Max	Mean
Chlorophyll A (ug/l/h)	-0.98	8.98	3.06
Total suspended solids (mg/l/h)	-4.06	3.79	1.63
Algae productivity (g/m^2/day)	-0.91	8.34	5.08

The elemental analysis of the Algal Biomass from three samples is shown in Table 7.

Table 7 - Elemental Analysis of Algal Biomass

Element	Week 3	Week 6	Week 8	Average
C%	55.0	51.0	47.2	**51.1**
H%	7.8	8.3	6.6	**7.5**
N%	9.1	9.37	6.69	**8.4**
O%	24.6	27.9	23.1	**22.8**

Based upon an average 51.1% carbon content of the algae, the algae carbon uptake at the mean productivity would be approximately 2.6 grams of carbon sequestration/m^2/day into the algal biomass. This would translate into a CO_2 uptake rate of about **9.5 g CO_2/m^2/day**. At the maximum algal productivity of 8.34 g/m^2/day, the carbon sequestration into the algal biomass would be 4.26 g C/m^2/day or **15.6 g CO_2/m^2/day**.

Based upon an average carbon dioxide uptake rate of 9.5 g/m^2/day, the proposed 40 acre algal cultivation system would sequester about **1.538 metric tons CO_2/day**. This observed uptake rate is significantly less than the 6.782 metric tons CO_2/day that was projected for algal productivity in the Hopewell wastewater.

The lower algal productivity observed in the Hopewell wastewater may have been due to a number of factors that were not obvious at the conception of the project.

1. The Hopewell wastewater is highly variable in terms of its organic and nitrogen loadings. During periods of high organic loading, dissolved oxygen levels were very low and hydrogen sulfide levels were detectable. These anoxic conditions are not conducive to algal growth. Vigorous aeration is required to maintain dissolved oxygen levels > 2 mg/L under these high loading conditions
2. The high organic loading also promotes vigorous bacterial activity. Although this activity should be stimulatory for algal growth through the evolution of dissolved carbon dioxide and the release of nitrogen nutrients, the microbial growth may also be inhibitory through competition for trace nutrients. It also produces a high turbidity that may interfere with photosynthetic efficiency due to reduced light penetration into the tanks. The algal growth medium was much darker than expected, especially under the anoxic conditions promoted by high organic loading
3. Although ammonia is a nutrient for algal growth, excess ammonia, especially under alkaline conditions, may be toxic to algae and in fact be inhibitory to growth. The organic compounds present in the Hopewell wastewater are high in organic nitrogen and ammonia levels were observed to increase significantly during high organic loading in the wastewater due to the mineralization of organic nitrogen by the bacterial populations in the cultivation tanks.

Figures 19 and 20 show the high turbidity present in samples of the Hopewell algal cultivation samples:

Figure 19 – Turbid Hopewell Algal/Bacterial Culture

Figure 20 – Hopewell Algal Tank with high turbid mixed algal/bacterial growth

2.3 CONVERSION OF ALGAL BIOMASS TO FUELS

One of the goals of the project was to evaluate the potential of the algal biomass cultivated in the Hopewell wastewater to be a feedstock for producing hydrocarbon fuels, such as green diesel and green jet fuel.

Samples of algal biomass were collected from the algal cultivation tanks at the end of the 5 day cultivation cycle and were shipped to UOP for fuel conversion studies. The algal biomass was converted to hydrocarbon fuels using a three step process.

1. The algal biomass was concentrated into a solid paste by centrifugation. The paste was dried at 105°C for a period of 12 hours to produce a solid material with a moisture content of between 10 – 15%
2. Thee dried algal biomass were liquefied using a proprietary UOP process. This process involved suspending the dried biomass in an organic solvent and processing the mixture at high pressure under a hydrogen atmosphere in the presence of a catalyst. Following liquefaction, the organic phase was separated from a liquid phase.
3. The liquefied organic phase was then subject to complete deoxygenation using the UOP/ENI Ecofining™ process.

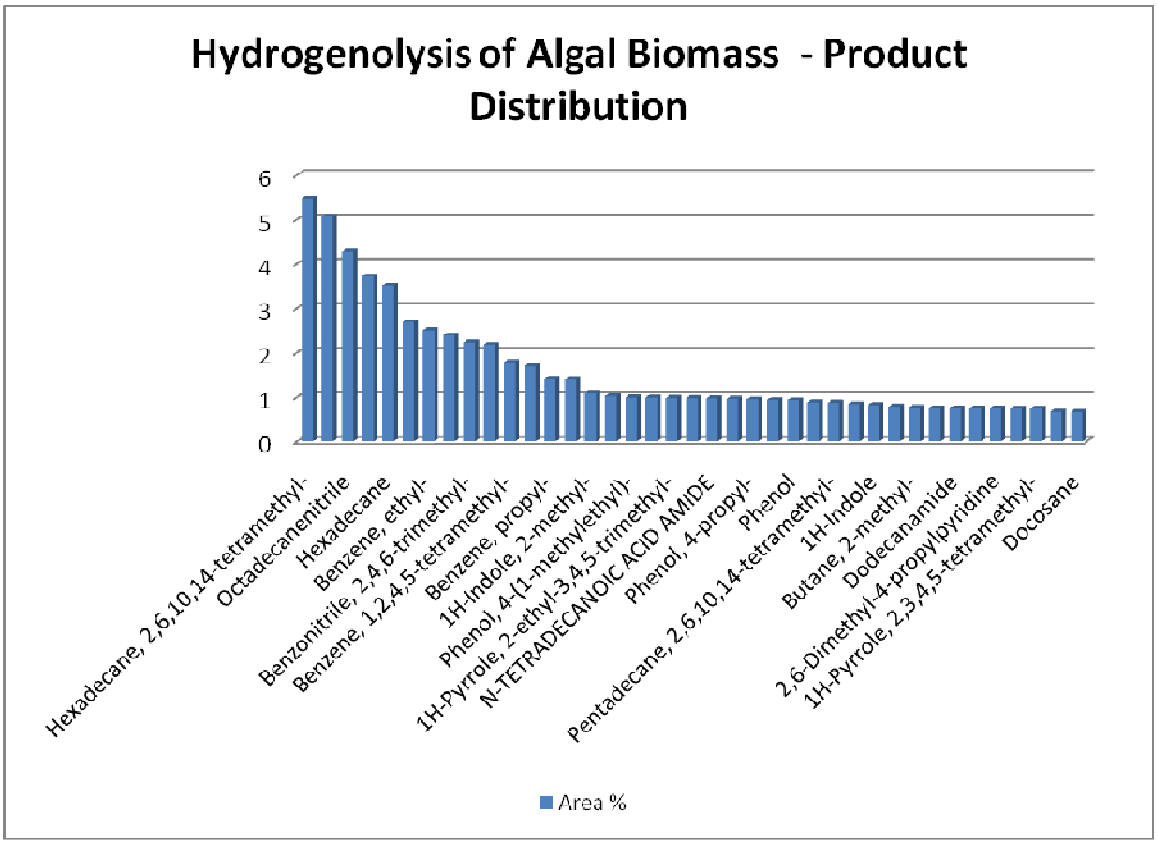
Table 8 below shows the yield and elemental composition of the product from the liquefaction and subsequent deoxygenation of Hopewell algal biomass.

Table 8 - Elemental Analysis of Products from Liquefaction and Deoxygenation of Algal Biomass

Element	Algal Biomass	Liquefied biomass	Deoxygenated Hydrocarbon Product
C%	55.0	88.1	86
H%	7.8	9.04	14
N%	9.1	0.77	<0.1
%O	24.6	0.15	<0.1

The hydrogenolytic liquefaction of the algal biomass significant reduced both the oxygen and nitrogen content of the original algal biomass and converted the solid algal biomass into a liquid organic product. The composition of the liquefied organic product is shown in Figure 21.

Figure 21 – GC-MS analysis of Liquefied Algal Organic Product



The liquefied product had a dark coloration and still contained significant quantities of oxygenates such as phenolics and nitrogenous organic species such as indoles, pyridines and pyrroles. These residual nitrogen and oxygenates species make the liquefied organic material unsuitable as a hydrocarbon fuel feedstock. Therefore, futher upgrading of this product was conducted using a deoxygenation step based upon the UOP Ecofining process. This process is a hydrotreatment using a fixed bed catalyst in a reactor in the presence of hydrogen at high pressure to remove the residual nitrogen and oxygenates from the liquefied product.

The deoxygenation product had a greatly reduced color and GC-MS analysis showed that it contained very few oxygenates and nitrogen-containg organic species (Figure 22). The major components of the deoxygenated liquefied algal product were n-paraffins and iso-parafins with carbon number C9 through C24 as shown in the following figure. The major components were in the C14 to C22 range, which would classify the deoxygenated algal hydrocarbon product as a heavy diesel. The high paraffinic content would give this fuel a high cetane value and it would be an excellent blending component to upgrade lower cetane petroleum diesels. One interesting and abundant constituent of the fuel is phytane (2,6,10,14-tetramethyl hexadecane), a diterpenoid alkane derivative of chlorophyll and other pigments present in the algal cells. This alkane is not typically present in renewable diesel derived from deoxygenation of the fatty acids associated with triglyceride feedstocks. The high degree of branching would indicate that the diesel product would have favorable cold flow properties.

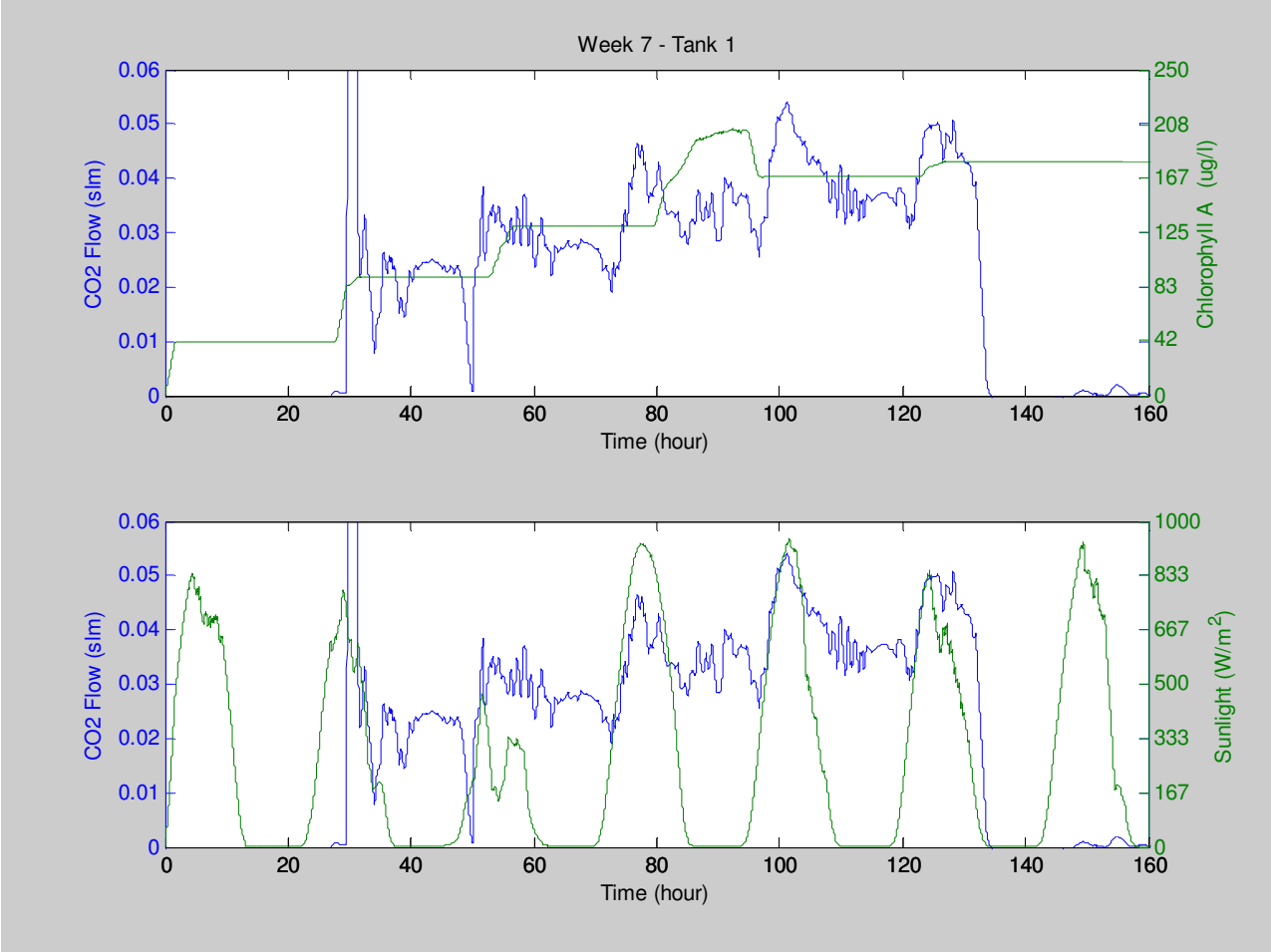
2.4 INTERACTIONS AMONG SYSTEM VARIABLES

2.4.1 CONTROLLED AND UNCONTROLLED CARBON DIOXIDE ADDITION

One of the key objectives of the Hopewell Phase 1 project was to show that the Honeywell sensors and control system could be used to more efficiently provide CO_2 for algal cultivation on an "added as need" basis rather than based solely upon pH as an indirect measurement of dissolved CO_2 availability.

Online sensing of both pH and dissolved CO_2 demonstrated that there is complex interaction based upon the speciation of carbonic acid and bicarbonate. Figure 22 below shows the addition of CO_2 to the algal cultivation tanks based upon pH control alone.

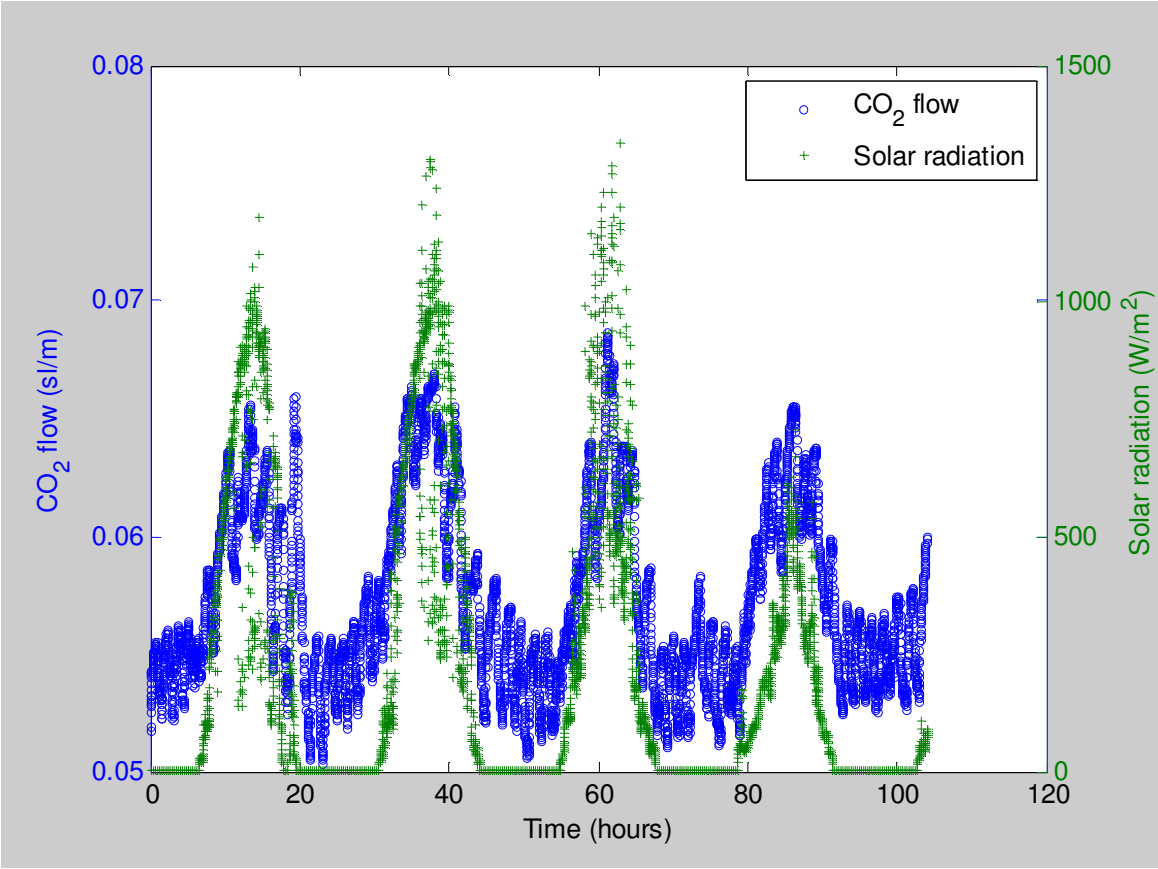
Figure 22 – CO_2 addition to Algal Cultivation Tank based upon pH Control



This results in a continuous addition of CO_2 to maintain a set pH value in the tank. The CO_2 addition rate increases in a stepwise fashion while the concentration of algal biomass, as measured by chlorophyll increases over a 5 day test period. Carbon dioxide is added even during periods of non-illumination for pH control.

When CO_2 addition is switched from control by pH but rather by direct measurement of dissolved CO_2 there is a direct correlation between illumination and CO_2 addition as shown in Figure 23.

Figure 23 - CO_2 addition to Algal Cultivation Tank based upon direct dCO_2 Concentration

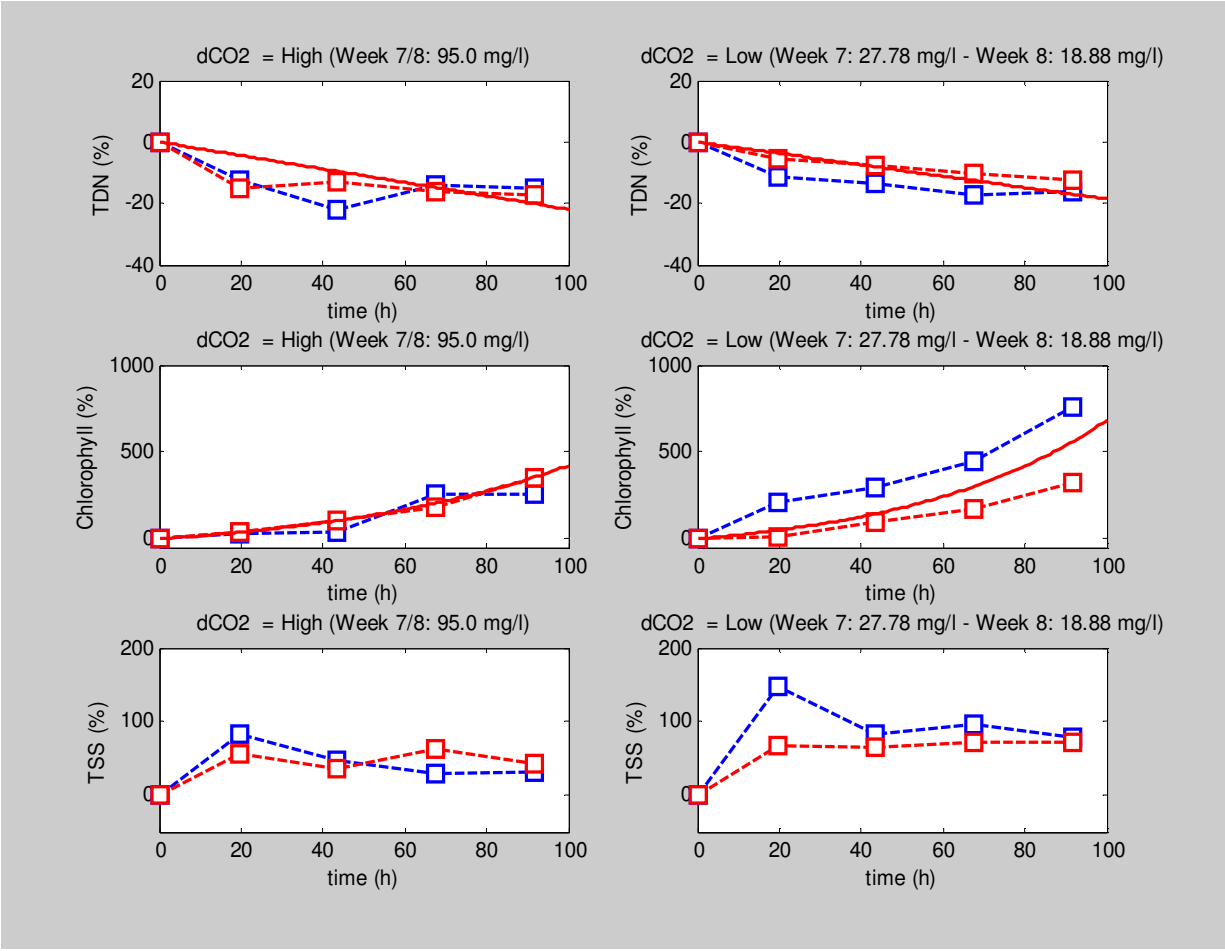


The implications of controlling CO_2 addition based upon direct measurement of dissolved CO_2 rather than indirect measurement via pH is that CO_2 addition can be performed much more efficiently. Significantly less CO_2 is lost to the system either via out-gassing to the atmosphere or via formation of dissolved bicarbonate/carbonate species lost to the system in the outflow of pond effluent water.

Keeping the dissolved CO_2 concentration above limiting levels is essential for optimal algal growth rates. Two levels of dissolved CO_2 were tested during the experimental phase. The low dissolved CO_2 experimental trials were performed at a constant pH and a dissolved CO_2 equal to the concentration of CO_2 in equilibrium with the wastewater at a pH of 7. The high dissolved CO_2 trial was performed using a dissolved CO_2 concentration of 95mg/l and pH of 7.

Figure 24 shows the effect of dissolved CO_2 on TDN, Chlorophyll A and TSS with other factors kept at nominal values. There is no clear indication that any of these variables was enhanced by higher levels of dCO_2.Chlorophyll growth was slightly lower at high dissolved CO_2 which might result from a negative effect of high CO_2 levels or a high salinity level after NaOH addition. This result suggests that the dissolved CO_2 concentration in equilibrium with the Hopewell wastewater at a pH of 7 was already in excess and not a limiting factor for algae growth at the algae biomass concentrations used in the experimental trials.

Figure 24 - Effect of Dissolved CO_2 on Total Suspended Solids, Chlorophyll and Total Dissolved Nitrogen.



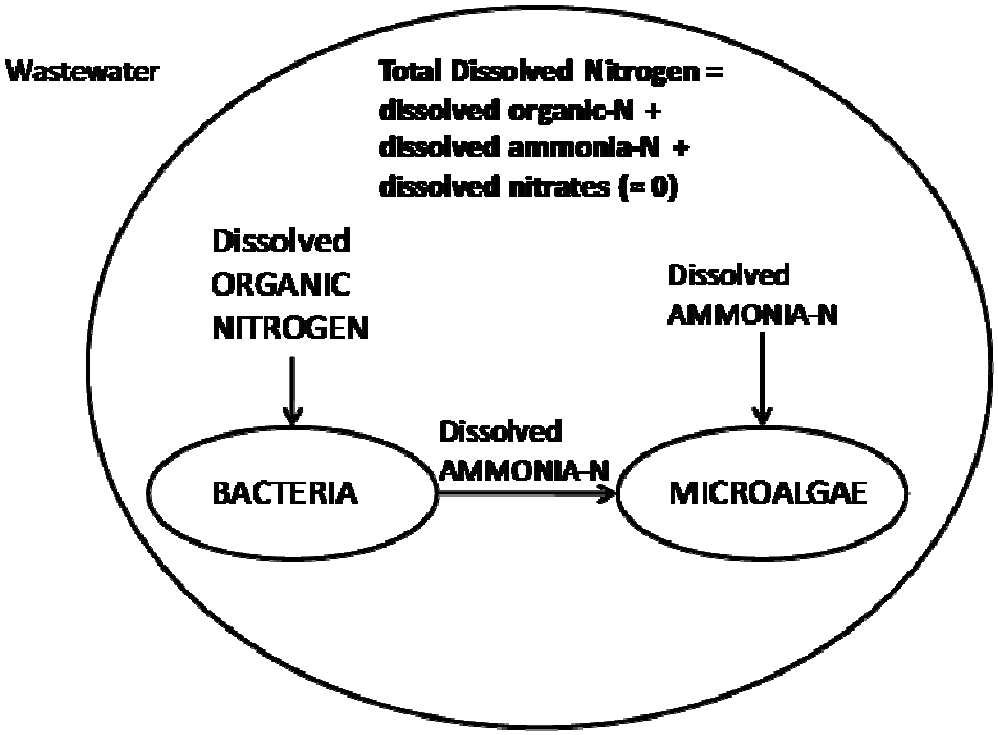
There is complex interplay in the Hopewell wastewater between the endogenous production of both CO_2 and inorganic nitrogen produced from bacterial activity and the uptake of these components by algae. It appears that dissolved carbon dioxide is generally not limiting in the Hopewell wastewater due to the continuous evolution of CO_2 from microbial activity.

2.4.2 Nitrogen Interactions during Algal Cultivation

A very complex interaction was observed between nitrogen generation and consumption in Hopewell wastewater due to the high level of organic and inorganic nitrogen and both bacterial and algal metabolic activity. With the Hopewell wastewater having a highly concentrated organic nitrogen component, rapid decomposition of organic nitrogen into inorganic nitrogen was observed. The nitrogen bounded to organic molecules, such as caprolactam, was decomposed by bacteria to produce ammonia-N (NH_3 and NH_4^+).

In an ideal algae wastewater remediation system, the nitrogen for algae consumption is dissolved in an inorganic form such as ammonia-N. In practice however, additional nitrogen becomes available as organic nitrogen (nitrogen bounded to organic molecules) is converted to inorganic nitrogen by bacterial activity.

Figure 25 - Schematic drawing of nitrogen cycle in the 'ideal' bacterial-algae combined system.



In the presence of high organic nitrogen, total nitrogen concentration in the filtrated solution (TDN) dropped due to rapid bacterial growth. The main driver for the nitrogen reduction was incorporation into bacterial biomass. The rapid bacterial growth incorporated more nitrogen than was produced as ammonia-N and therefore the filtrated solution had a lower nitrogen concentration. Figure 26 and Figure 27 show the correlation between measured TDN, dissolved organic nitrogen and Ammonia-N. Blue, black and red circles are used to indicate measured data for the experimental weeks where the initial dissolved organic nitrogen concentration was high (i.e. week 4, 5 and 6).

When organic nitrogen was in low concentrations or depleted, the bacterial growth rate diminished. However, ammonia-N was still produced by the remaining bacterial biomass. The change in TDN was therefore the remaining balance of ammonia-N produced by bacteria and that consumed by algae biomass. As shown in Figure 27,, when organic nitrogen concentration was low (green circles), total dissolved nitrogen was proportional to the ammonia-N concentration.

Figure 26 - Correlation between measured TDN and dissolved organic nitrogen. Blue circles: week 5, black circles: 6, red circles: week 4, green circles: week 1 to 3 and 7 to12 and 6.

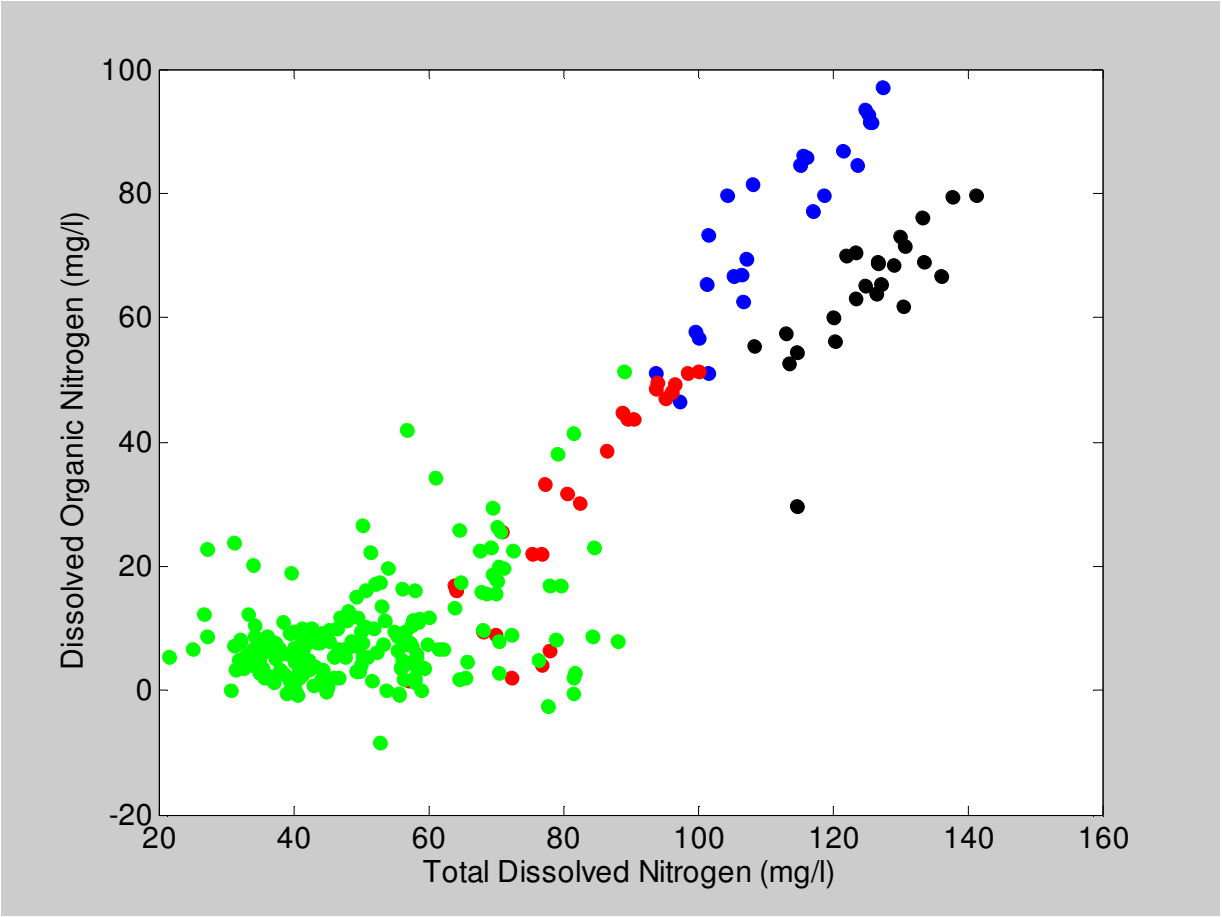
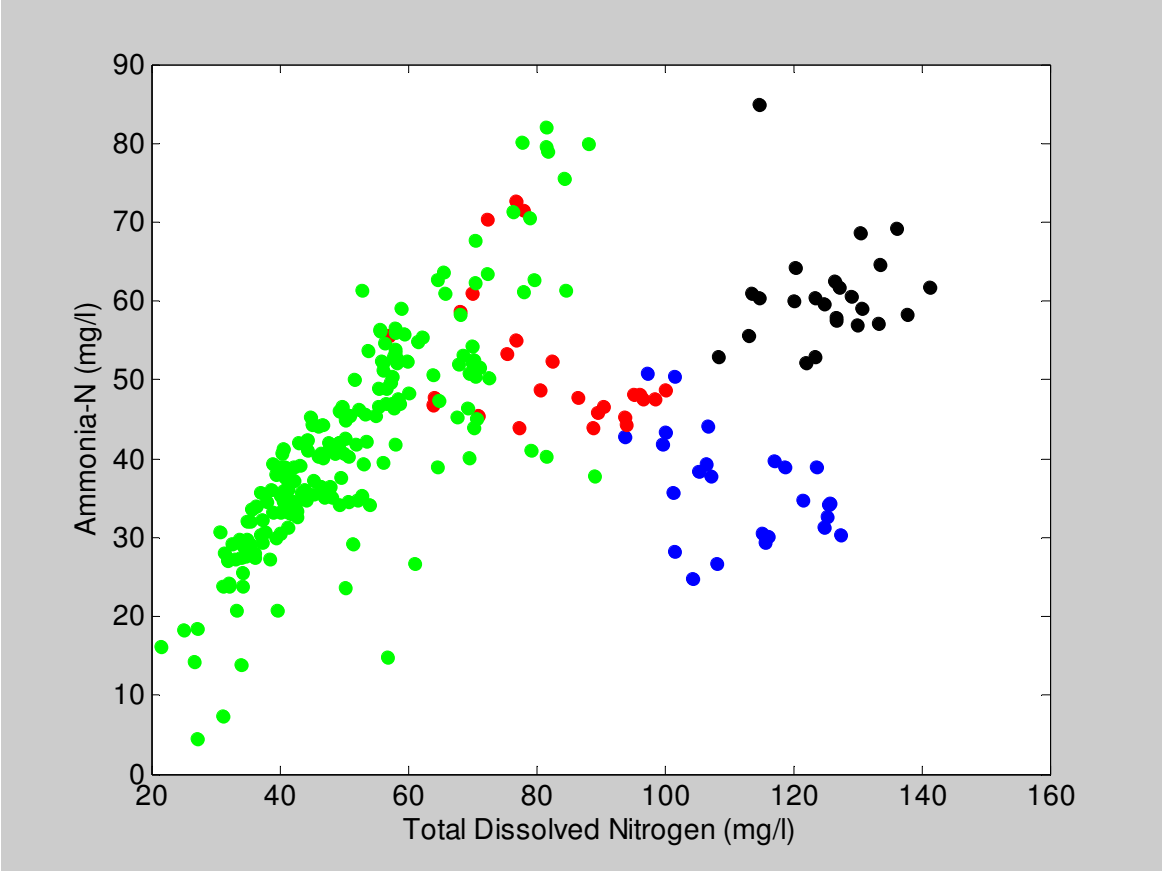


Figure 27 - Correlation between measured TDN and Ammonia-N. Blue circles: week 5, black circles: 6, red circles: week 4, green circles: week 1 to 3 and 7 to12 and 6.



2.4.3 INTERACTIONS AMONG TOTAL DISSOLVED NITROGEN, CHLOROPHYLL A AND TSS

Figure 28 shows the relationship between TDN and Chlorophyll A. The figure suggests that within the 10% algae innoculum used in the experimental trials, there was no definite trend between changes in total dissolved nitrogen and Chlorophyll A. Figure 29 shows the correlation between changes in total dissolved nitrogen and non-algae total suspended solids. Under conditions of high organic nitrogen (weeks 4, 5 and 6), Figure 29 indicates a strong correlation between the growth of non-algae total suspended solids and the reduction in dissolved nitrogen. Such correlation also exists with low organic nitrogen; however, due to the low initial organic nitrogen concentration, a smaller amount of nitrogen was consumed and retained in the bacterial biomass. About 90% of the total biomass was in the form of non-algae biomass.

Figure 29 - Correlation between percent change of TDN and Chlorophyll A

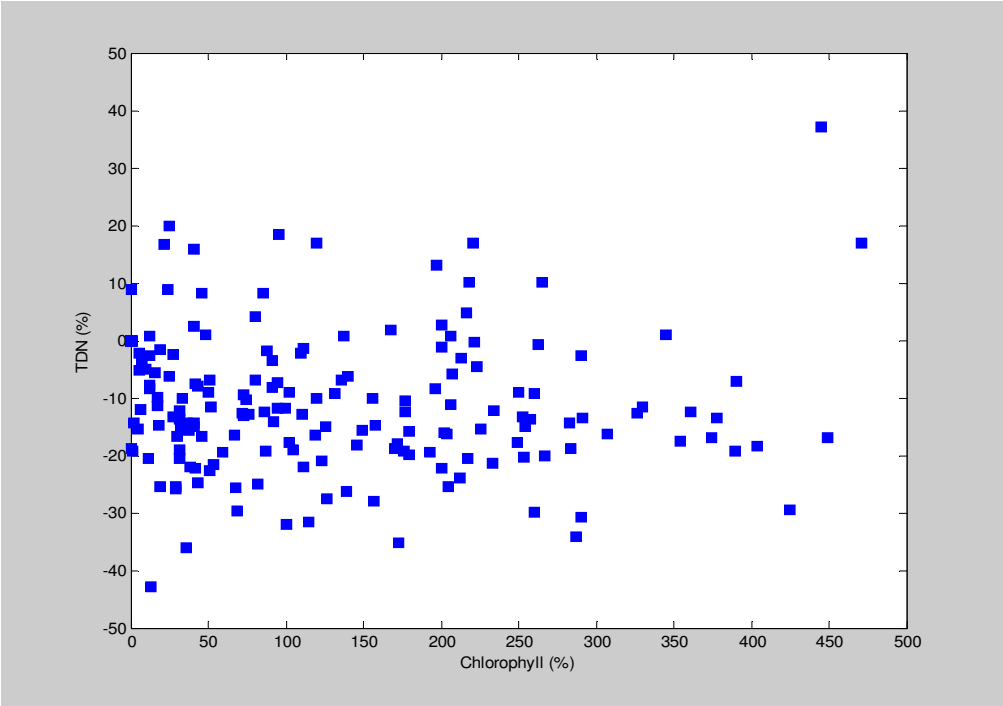
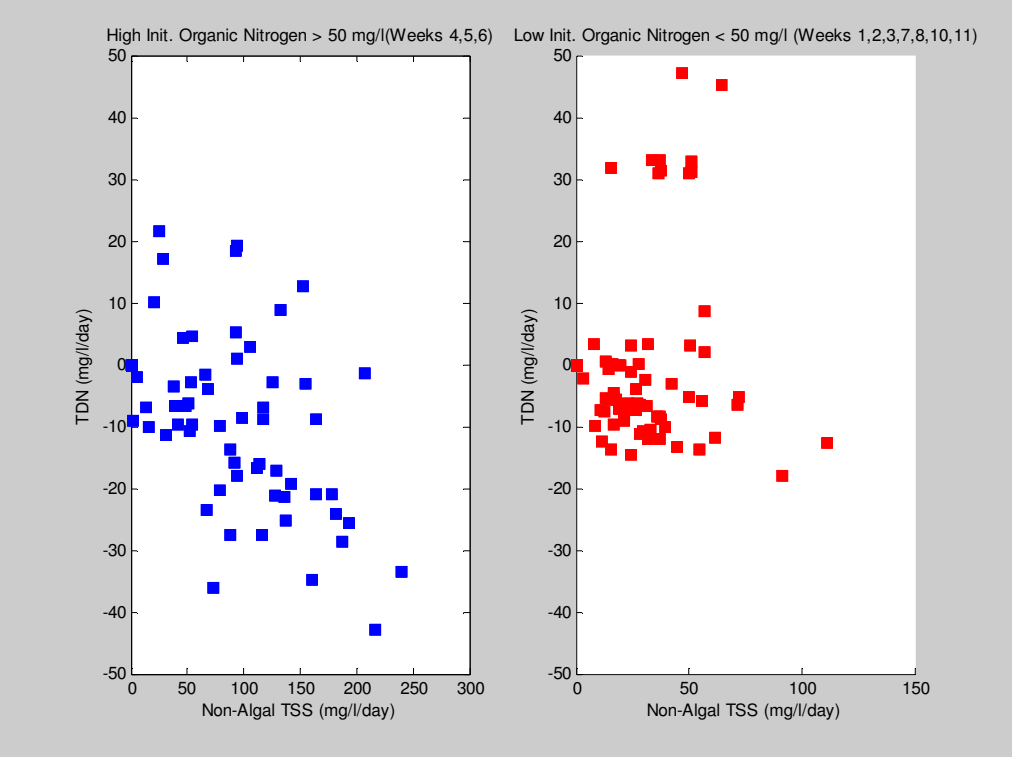


Figure 30 - Correlation between absolute changes in TDN and total suspended solids



2.4.4 TEMPERATURE EFFECTS

The effect of temperature on biochemical reactions in microorganisms is one of the most important factors influencing algae and non-algae growth rates. Three levels of temperature were used in the experimental trials: 10, 20 and 30 deg C. Figure 31 shows the effect of temperature on Chlorophyll A with other factors at nominal values. Chlorophyll A shows a clear increase with temperature. Minimal growth was observed at 10 deg while the highest rate was obtained at 30 deg C. From the best exponential approximation of the algae growth, an algae specific growth rate of 0.4176 day-1 (e.g. the algae double their biomass every 39.8 hours or 1.66 days) was obtained at the highest temperature. Figure 30 shows that within the 5-day experimental period, algae cells were entering the exponential growth phase.

Figure 31 shows the impact of temperature on TSS with other factors at nominal values. TSS shows a clear increase with temperature. Like Chlorophyll A, there was minimal increase at 10 deg and the maximum rate (82.85 %/day) was obtained at 20 deg C. The 30 deg C experiment was not performed in week 7. The low TSS growth in week 7 at 20 deg C can be explained by a limited initial concentration of organic nitrogen which was consumed almost entirely in the first days of experiments (data not shown). After the organic nitrogen was depleted, TSS increase was the result of a higher algae biomass.

Figure 32 shows the effect of temperature on TDN with other factors at nominal values. Solid red lines represent the best linear approximation. Linear rates are only valid within a 5-days period and are used only as a guideline to assess the effect of each factor on TDN. Changes in TDN are the result of algae and non-algae biological metabolisms and a linear approximation might not be adequate in all cases. The percent nitrogen reduction averaged 5.27 %/day at 20 deg C.

Figure 30 - Effect of temperature on Chlorophyll A

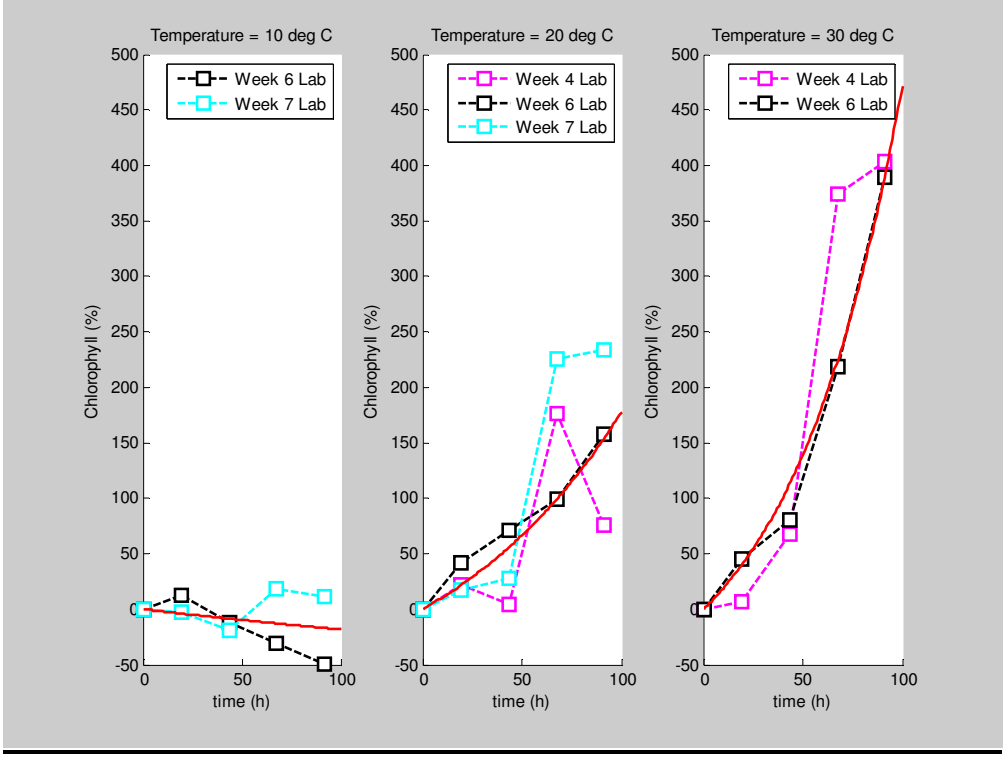


Figure 31 - Effect of temperature on total suspended solids

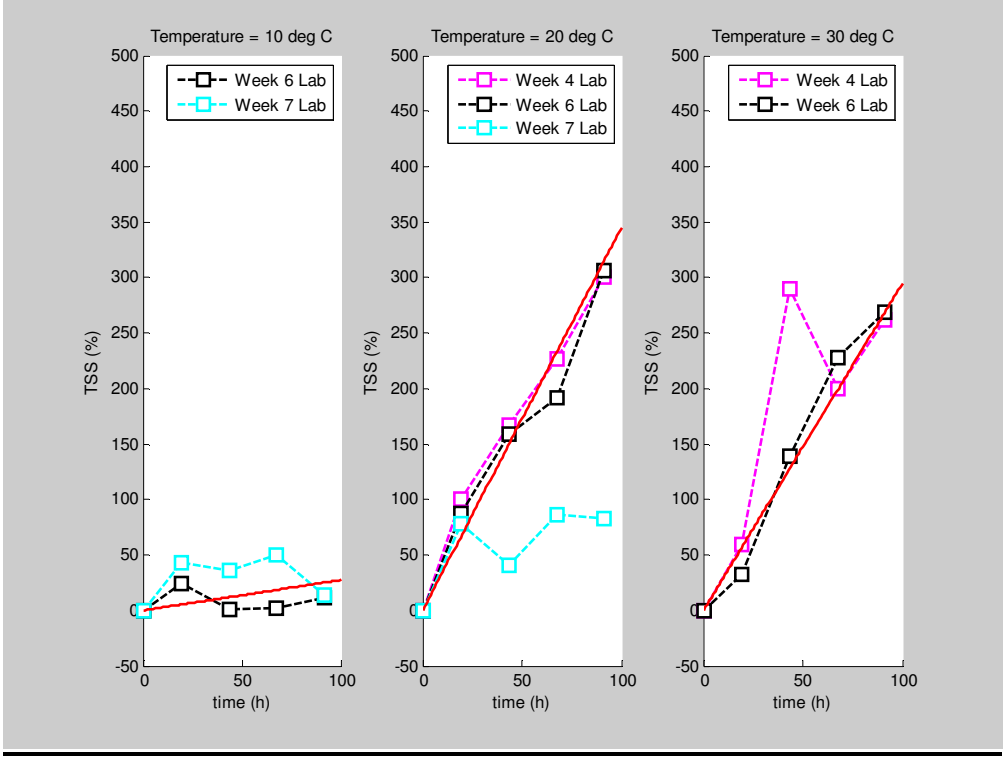
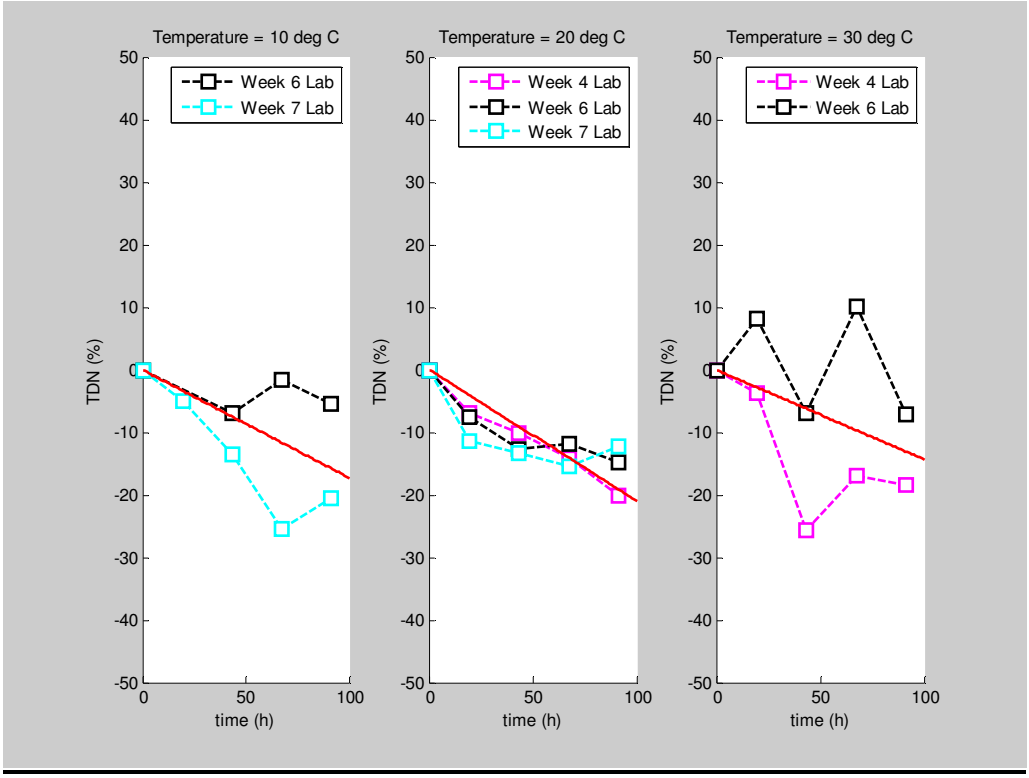


Figure 32 - Effect of temperature on total dissolved nitrogen



2.4.5 EFFECTS OF PH

Along with temperature, pH can also affect growth rate of algae and non-algae biomass. Three levels of pH were used in the experiments: 6, 7 and 8.5. Figure 33 shows the effect of pH on Chlorophyll A. The figure shows a higher growth rate with increasing pH. Minimal algal growth was achieved at pH of 6 while the maximum rate was obtained at a pH of 8.5 (0.2856 day-1); there was little difference between pH of 7 and 8.5.

Figure 34 shows the effect of pH on TSS. The figure indicates that TSS grows fastest at higher pH values, although the growth difference between pH 7 and 8.5 is not clear from the experimental results. 82.85 and 88.07 % per day TSS increases were achieved at pH of 7 and 8.5, respectively.

Figure 35 shows the impact of pH on TDN. The percent nitrogen reduction averaged 5.27 %/day at 20 deg C.

Figure 33 - Effect of pH on Chlorophyll A

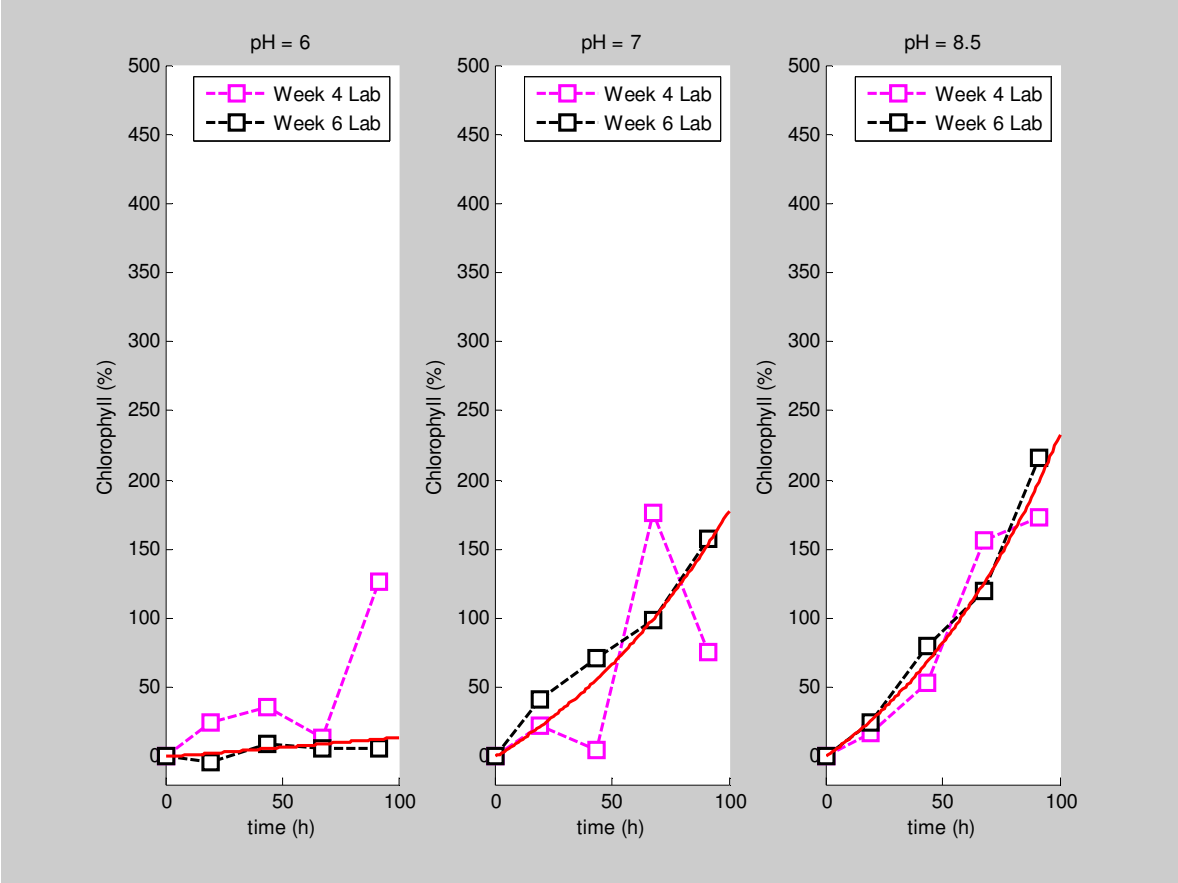


Figure 34 - Effect of pH on Total Suspended Solids

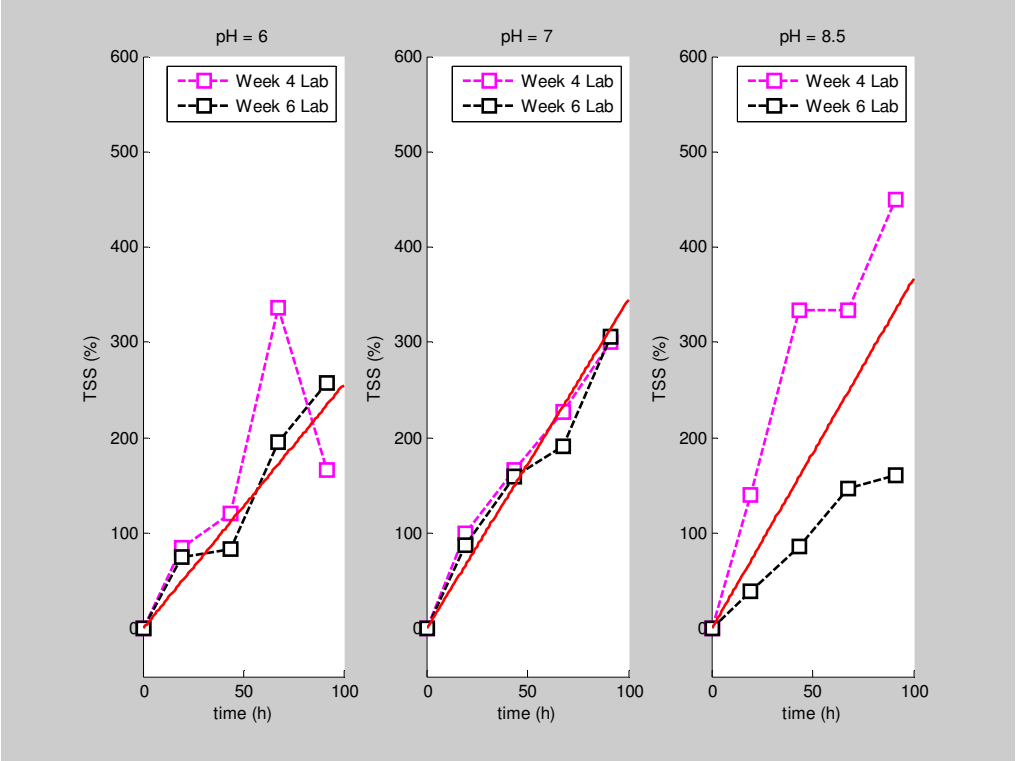
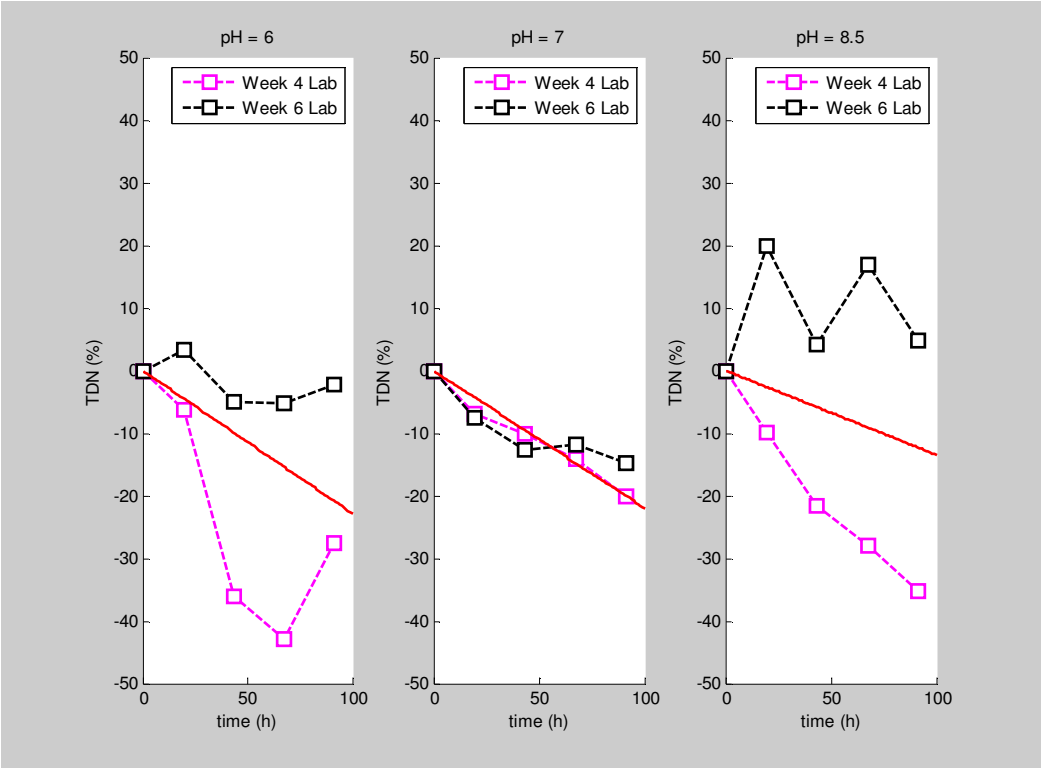


Figure 35 - Effect of pH on total dissolved nitrogen

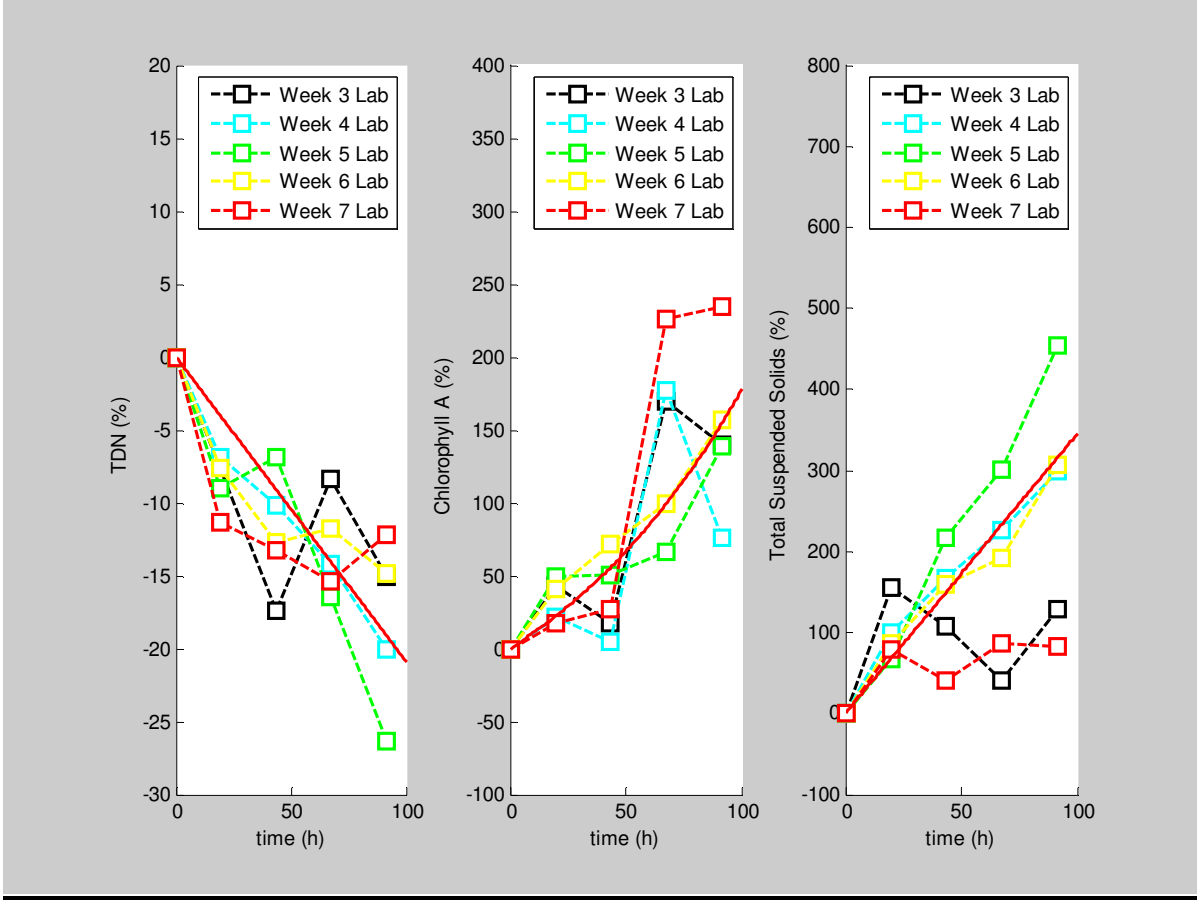


2.4.6 EFFECTS OF UNCONTROLLED FACTORS

Factors such as sunlight and initial nitrogen concentration (organic and inorganic) were not constant during the experimental trials. These uncontrollable factors can also affect the biomass growth and nutrients uptake rate.

The effect of uncontrollable factors is analyzed using the *control* trial where all the controlled parameters were kept at the nominal values (i.e. temperature = 20 deg C, pH= 7 and N:P ratio = 10:1). Figure 36 shows the biomass growth and nitrogen uptake rate in the 'control' tank for the different weeks of experimentation.

Figure 36 - Nitrogen uptake and biomass growth rate in 'control' trials



SUNLIGHT

Light is an essential requirement for algae photosyntesis. Daily variability in sunlight intensity due to weather conditions can affect algae growth rate significantly. Figure 37 shows the variation in total sunlight as well as sunlight hours for the 12 weeks of experimentation. Sunlight data for weeks 1 to 5 were not included as the sunlight sensor gave erroneous measurements at high light intensities and had to be replaced. To overcome this difficulty, total sunlight hours were used instead of total sunlight energy to assess the effect of sunlight on algae growth. Figure 37 also shows a linear correlation between total sunlight hours and total sunlight energy.

The effect of sunlight on TDN and biomass growth rate in the control trials is shown in Figure 38. For the range of total sunlight hours available during the experimental trials, algae biomass did not show any significant increase with sunlight. The control experiments were run mainly in May and June; therefore further experimental runs throughout the year are required to assess the effect of sunlight on algae biomass growth.

Figure 37 - Sunlight intensity vs. week of experimentation

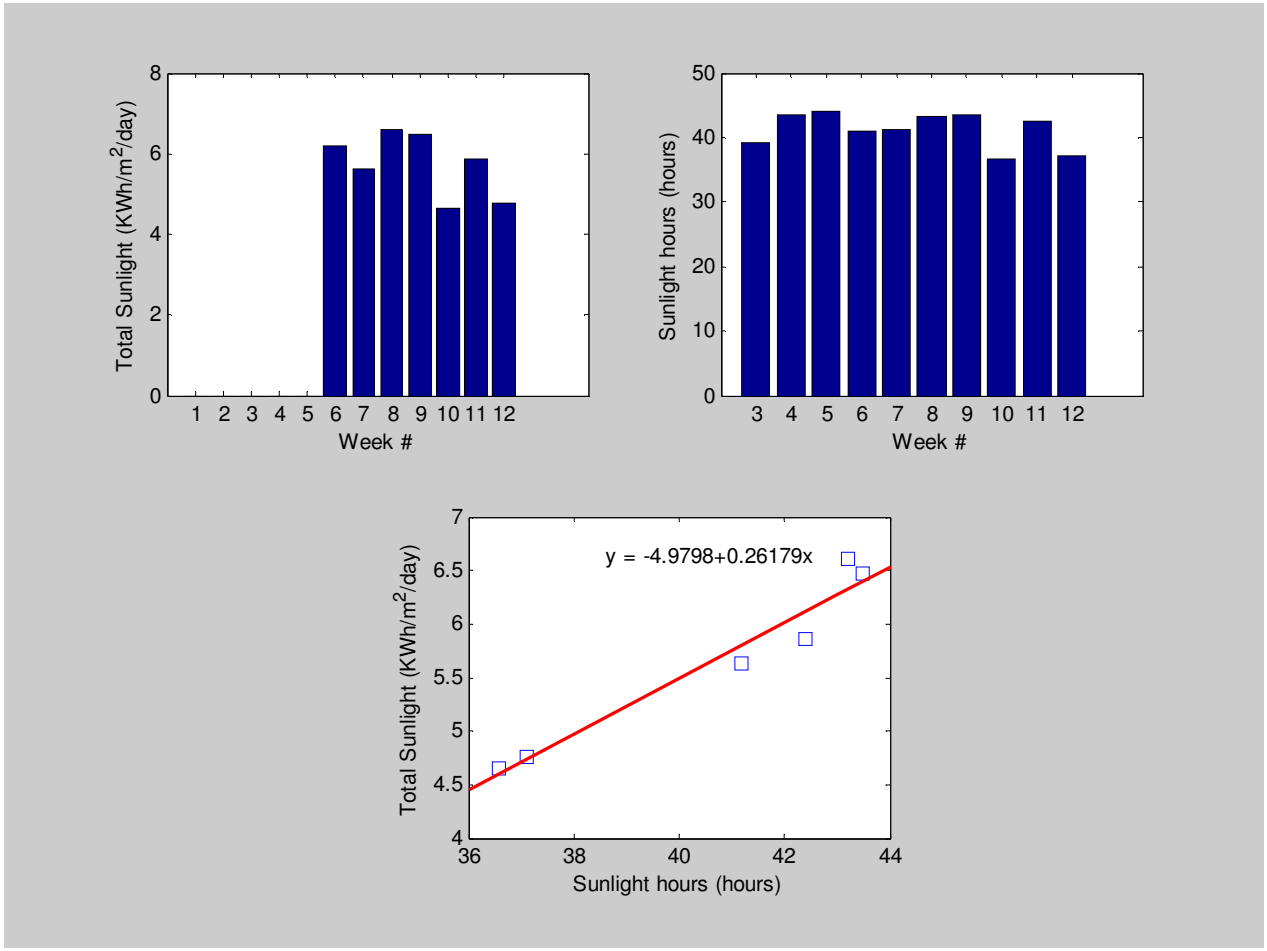
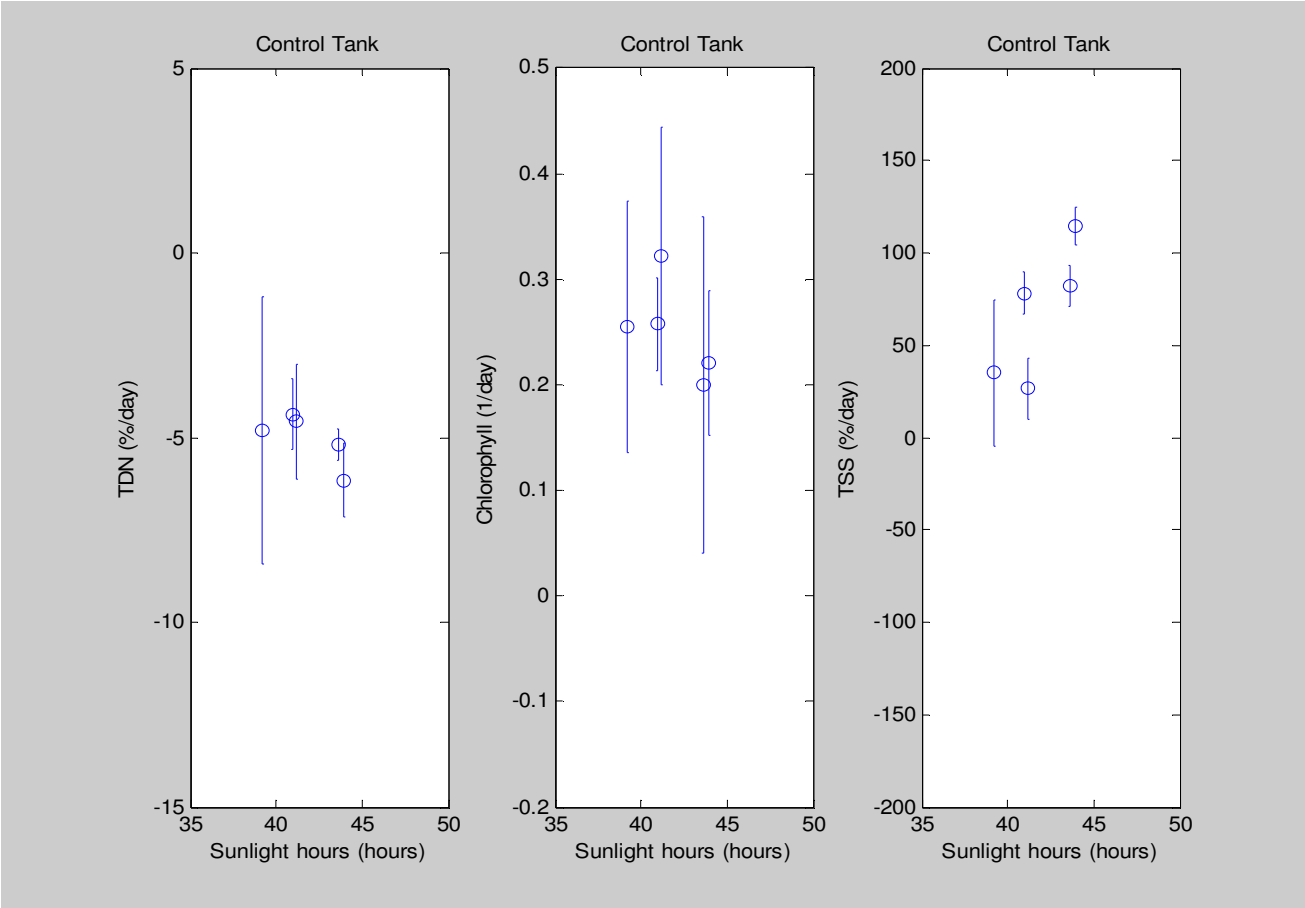


Figure 38 - Effect of sunlight hours on TDN, Chlorophyll A and TSS in the 'control' experiment. Error bar represents 95% confidence interval.



INITIAL NITROGEN CONCENTRATION

Initial nitrogen concentration was an uncontrollable factor that varied from week to week. All batch experiments run within the same week had the same initial nitrogen concentration; however, there were weekly variations due to fluctuations in the Hopewell wastewater effluent.

Figure 39 shows the initial total and organic dissolved nitrogen concentration as a function of week of experimentation. Due to fluctuations in the wastewater composition, high dissolved organic nitrogen compositions were used in the experimental tanks in weeks 1 to 6 (with very high concentrations on weeks 4, 5 and 6) and low concentrations from weeks 7 till 12. Figure 40 shows the effect of initial organic nitrogen concentration on TDN, Chlorophyll A and TSS in the control trials. Initial concentration of organic nitrogen shows a clear effect on total suspended solids. High dissolved organic nitrogen concentration led to a faster growth of TSS. Initial dissolved organic nitrogen, however, did not affect the growth rate of algae biomass (Chlorophyll A).

Figure 39 - Total and Organic dissolved nitrogen concentration in the wastewater at the beginning of the experimental week.

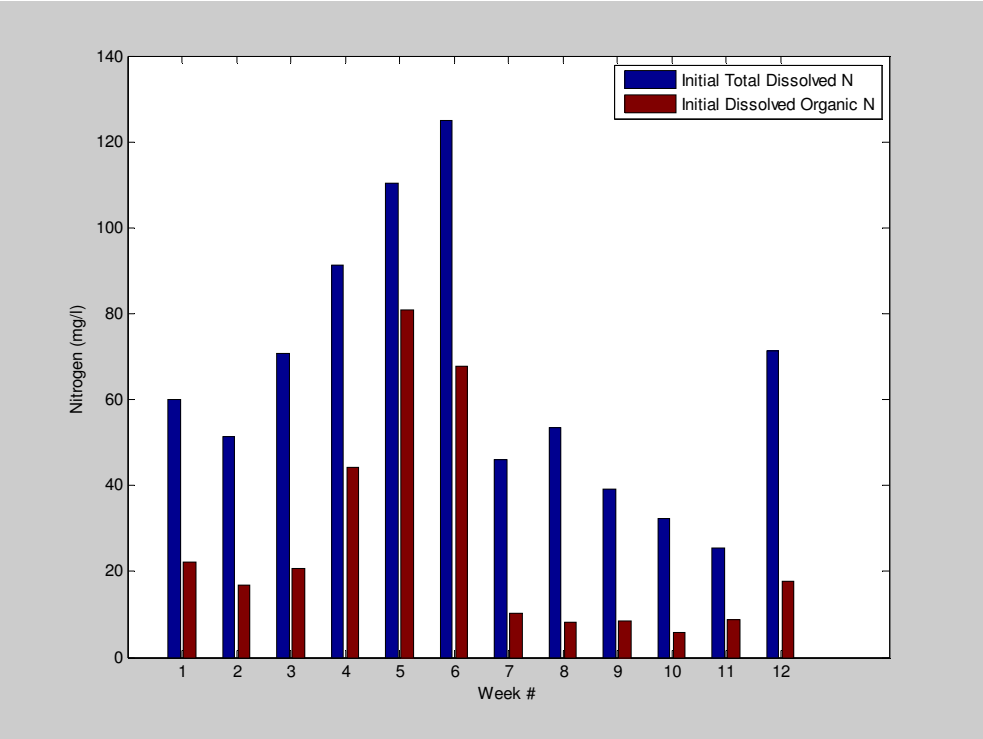
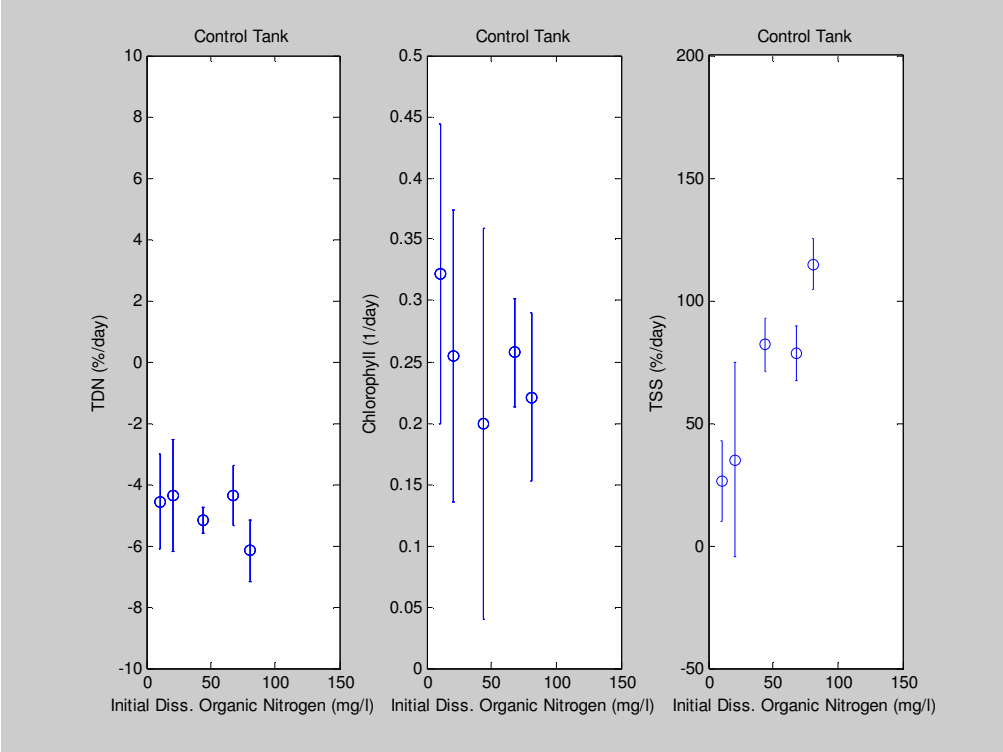


Figure 40 - Effect of initial dissolved organic nitrogen on TDN, Chlorophyll A and TSS in the 'control' experimental trials. Error bar represents 95% confidence interval.



3. CONCLUSIONS

The accuracy of pH, dissolved O_2, dissolved CO_2, turbidity, Chlorophyll A and conductivity online sensors is suitable for process control of algae cultivation in an open pond. Some sensor measurements in waste water, notably dissolved CO_2, appear to be more accurate than the lab technique used. Bio-fouling of the sensors was not an issue in Phase 1 due to the fact that sensors were rinsed and moved from tank to tank every couple of hours. Finally, the online sensor repeatability and response time are suitable for process control given the timescale of the chemical and biological processes involved in algae cultivation.

Collected data indicates wide fluctuations in the Hopewell wastewater nitrogen concentration. Experiments performed with high organic nitrogen levels showed that bacterial activity was the main driver to convert dissolved organic nitrogen to biomass and therefore reduce the concentration of total nitrogen in the filtrated solution. With 10% algae inoculum used in the experimental trials, a small fraction of the initial total nitrogen was incorporated into the algae biomass. Luxurious bacterial nitrogen uptake when the organic nitrogen in solution was high, led to a reduction of total dissolved nitrogen concentration.

For a continuous remediation system, separate bacterial pre-treatment, algal inoculum and cultivation systems are needed. A two-stage process can be designed to first transform organic nitrogen into ammonia-N and then grow algae, incorporate inorganic nitrogen into algae biomass and maximize algae yields, thereby increasing CO_2 uptake.

Since dissolved organic nitrogen concentration in the Hopewell wastewater effluent is variable and depends on upstream conditions, active control of residence times is critical to allow bacteria to maximize the conversion of organic nitrogen into ammonia-N. Algae biomass concentration is also a critical parameter to maximize the subsequent algae nitrogen uptake. In a continuous production system, control of residence time and algae biomass concentration are therefore important to achieve desired levels of nitrogen reduction and algae biomass production.

From the experimental trials, it was found that bacteria and algae biomass show the highest rate of growth at 30 deg C and minimal growth at 10 deg C. Algal specific growth rates of 0.2448 and 0.4176 day-1 were obtained at 20 deg C and 30 deg C, respectively. Increasing pH from 6 to 8.5 led to an increase in algae activity with minimal difference between 7 and 8.5. Low pH and temperatures are not favorable for algae biomass cultivation.

Experiments conducted under high concentration of dissolved CO_2 did not enhance algae growth rate. This result suggests that the dissolved CO_2 concentration at a pH of 7 (nominal case) was already above limiting value. Even though dissolved CO_2 did not show a positive effect on biomass growth, controlling its value at a constant set-point during daylight hours can be beneficial in an algae cultivation stage with high algae biomass concentration to maximize the rate of CO_2 uptake.