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Recycling Produced Water for Algal Cultivation for Biofuels

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ABSTRACT

Algal growth demands a continuous source of water of appropriate salinity and nutritional content. Fresh water sources are scarce in the deserts of the Southwestern United States, hence, salt water algae species are being investigated as a renewable biofuel source. The use of produced water from oil wells (PW) could offset the demand for fresh water in cultivation. Produced water can contain various concentrations of dissolved solids, metals and organic contaminants and often requires treatment beyond oil/water separation to make it suitable for algae cultivation. The produced water used in this study was taken from an oil well in Jal, New Mexico. An F/2-Si (minus silica) growth media commonly used to cultivate *Nannochloropsis salina 1776* (*NS 1776*) was prepared using the produced water (F/2-Si PW) taking into account the metals and salts already present in the water. *NS 1776* was seeded into a bioreactor containing 5L of the (F/2-Si PW media. After eleven days the optical density at 750 nm (an indicator of algal growth) increased from 0 to 2.52. These results indicate algae are able to grow, though inhibited when compared with non-PW media, in the complex chemical

conditions found in produced water. Savings from using nutrients present in the PW, such as P, K, and HCO_3^-, results in a 44.38% cost savings over fresh water to mix the F/2-Si media.

INTRODUCTION

Alternative fuel sources, such as algae-based biofuel, are essential to our national energy security. Without fuel our military, economy, and our freedom to travel are in jeopardy. Algal biofuel production can provide a supplement to fossil fuel demands as well as provide methane for power plant combustion[i] and other valuable co-products. Algal biofuel is rather versatile and can be used anywhere from your car, to diesel trucks, to jet-fuel.[ii]

Algae cultivation in raceway ponds requires ample sunlight. Sunlight is abundant in the deserts of the Southwestern United States, yet, fresh water is scarce. Three categories of water salinity have the potential to be considered for the available species of algae being considered for biofuel production: fresh water, brackish (5000 ppm total dissolved solids (TDS) to just under 35000 ppm TDS), and sea water (around 35000 ppm TDS). Fresh water constitutes 1% of the available water in the world and contains low levels, if any, of chloride, phosphorus, carbonate and potassium. As a result, these nutrients must be added to the media at an additional cost to cultivators. Sea water contains needed nutrients for marine alage, but is limited to coastal areas. Brackish groundwater water is widely available and due to its wide range of TDS, it is suitable for cultivation for many species of algae.

Produced water (PW) is often found to be in the brackish TDS range. The PW used in our study is approximately 15000 ppm TDS. Currently PW disposal costs oil producers $0.30 to $10.00 US per barrel.[iii] The PW in this study is relatively reducing which can affect chemical speciation and algal nutrient availability. However, with aeration the water can be brought to more oxidizing conditions better for media mixing and algal cultivation. We found through this study that algae can grow in PW[iv], although the growth kinetics appear to be affected.

Eldorado Biofuels

Eldorado Biofuels, owned by Paul Laur, is part of the National Alliance for the Advancement of Biofuels and Biotechnology (NAABB) near Jal, New Mexico. This company is currently treating PW (Figure 1) and using it for algal cultivation for biofuel production.[v] Eldorado Biofuels cultivates a mix of freshwater algae (*Scenedesmus* and *Tetracystis*) referred to as Jalgae ™, grown in a 10-50% PW solution mixed with fresh water (Figure 2). This symbiotic relationship provides oil well owners and the algae facility with fiscal savings on the disposal and acquisition of water respectively.

EXPERIMENTAL METHODS

From the preliminary data taken from Eldorado Biofuels, it is evident that algae are able to grow in at least some concentration of produced water. This experiment investigates growth of *NS-1776* in F/2-Si made with treated produced water (F/2-Si PW) in closed bioreactor system at the laboratory scale. This alga is commonly grown as a source of biofuel lipids in higher salinity waters.

The produced water from the Joyner well (Appendix B) was analyzed for constituents such as metals, anions, and organic compounds. Using this data, the concentration of intrinsic nutrients was subtracted from the original F/2-Si recipe and additional nutrients were added as necessary to make the F/2-Si PW identical.

Sediment, not less than 1 µm, pink in color, was filtered from the treated produced water before additional 0.2 µm filtration for bacterial sterilization. This sediment is thought to be the result of precipitates formed from high sulfate concentrations as shown from the scanning electron microscope (SEM) image and EDAX spectra (Figure 3). This indicates some loss of sulfate compounds which can remove nutrient metals from the media.

Algae are grown in a bioreactor. Initially five liters of F/2-Si PW are added. Artificial lamps (see Appendix A) light the system for sixteen hours per day (3 AM to 7 PM).

FIGURE 1—Produced water treatment facility at Eldorado Biofuels Jal, New Mexico. July 24, 2012.

FIGURE 2—Innoculation raceway pond at Eldorado Biofuels Jal, New Mexico. July 24, 2012.

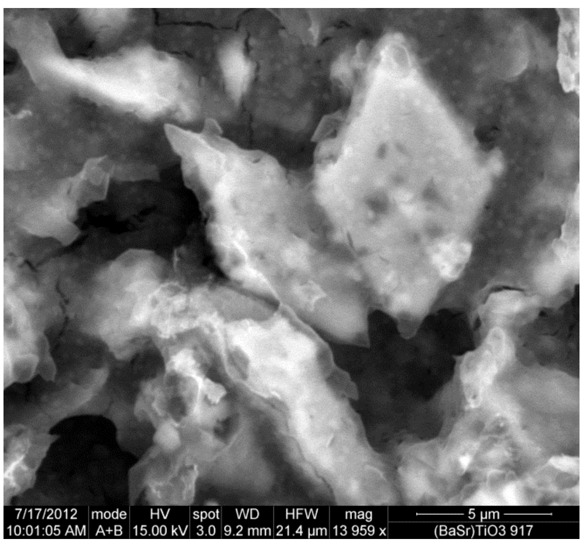
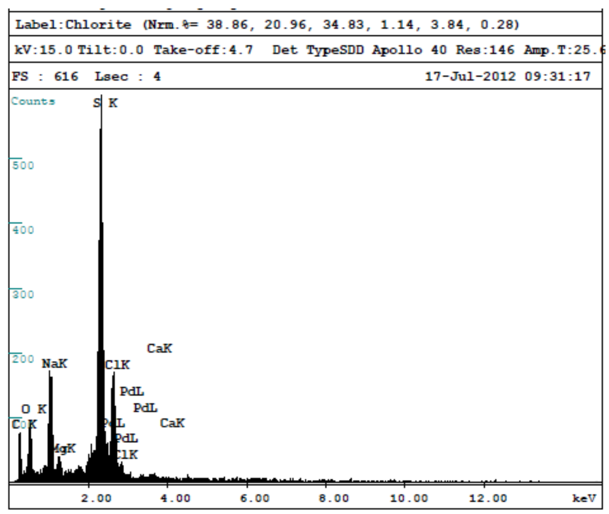


FIGURE 3—SEM with backscatter detector (above) of rhomboid like crystals recovered from 0.22 µm filter used in produced water filtration; 1 µm filter paper delivers the same precipatate. The spectrum (right) detects the presence of an element; quantification is reported directly below it.



EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	34.69	50.19	0.0420	1.0433	0.1160	1.0001
O K	21.91	23.80	0.0319	1.0236	0.1421	1.0003
NaK	13.86	10.48	0.0361	0.9553	0.2724	1.0010
MgK	2.21	1.58	0.0057	0.9785	0.2626	1.0015
S K	18.25	9.89	0.1307	0.9602	0.7432	1.0037
ClK	7.69	3.77	0.0379	0.9187	0.5364	1.0005
PdL	1.14	0.19	0.0076	0.7621	0.8786	1.0001
CaK	0.26	0.11	0.0018	0.9410	0.7355	1.0000
Total	100.00	100.00				

Gases including CO_2 (to maintain 8.2 pH), and O_2 (maintained 100% DO) are fed into the system; stirred at 400 rpm.

Water characteristics such as pH, dissolved oxygen (DO), and nitrate levels are continually monitored. Nitrate levels are monitored closely because when depleted, algae begin to produce more lipids; similarly to how we store fat during periods of starvation. Carbon dioxide is added on-demand to control the pH of the system to 8.2; as algae metabolize they increase the pH, CO_2 lowers it.

Optical density is monitored in the bioreactor from two wavelengths: 850 nm which is thought to be dependent more on lipid content, and 750 nm which is used as a proportion to cell growth. The 850 nm data is automatically recorded to the computer, however, the 750 nm data is taken by an autosampler every six hours and data is entered by hand.

RESULTS

An algal growth experiment using F/2 –Si in fresh water media in the same bioreactor, was compared with our experiment using F/2 –Si PW media (Figure 4). We found that there is a longer period which the algae takes to adjust and grow in the new conditions; growth in this period is typically slower and is referred to as lag phase. There is also noticeable difference between chlorophyll, optical density (OD), and the rate of change in nitrate levels; all indicative of fewer algae present and thus slower growth. This observation suggests that the PW used in this study is not chemically suited to optimal algal growth. Further water treatment is likey required.

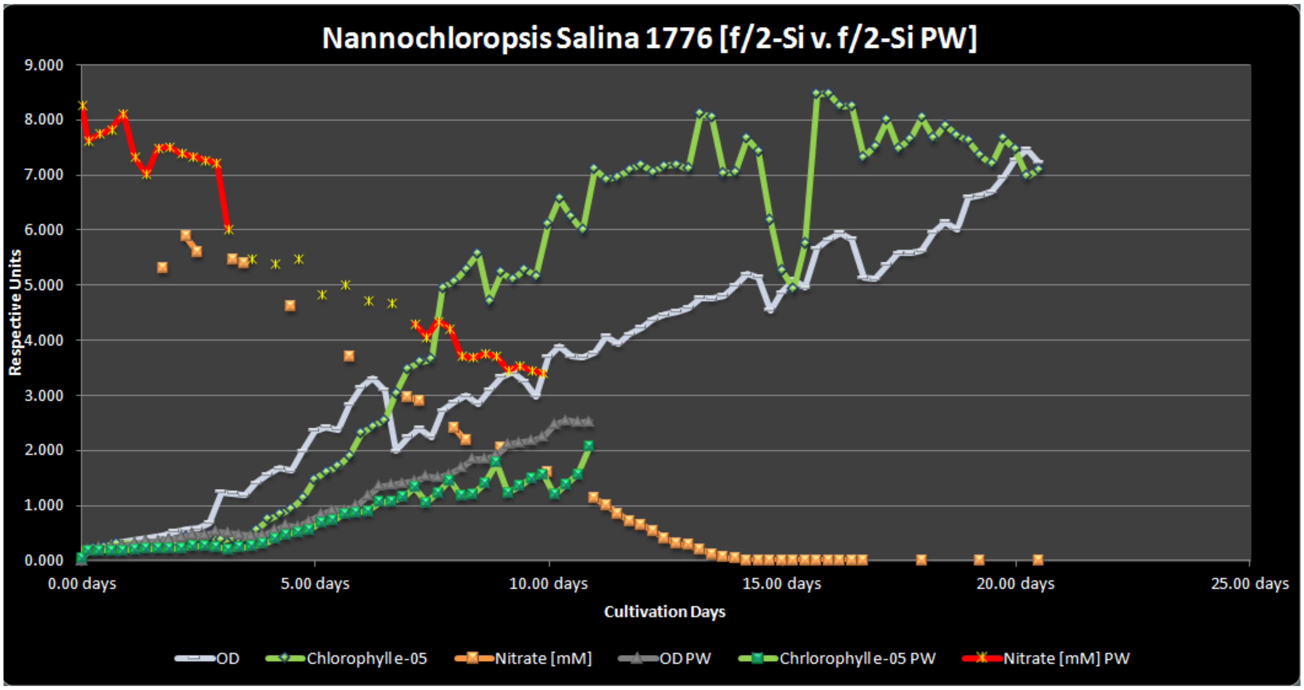


FIGURE 4—Comparison graph between F/2-Si without PW (light colors) and F/2-Si with PW. Graph shows noticeable lag phase, but growth nonetheless.

An analysis comparing the cost to produce 1000 L of F/2-Si using PW and FW (Table 1) revealed that for F/2-Si FW the cost was $55.03 USD and for a F/2-Si PW, $30.61 USD. The cost to produce F/2-Si using PW is 0.5562 times the cost to make F/2-Si FW; this also provides service to the Oil and Gas industry. This estimation included the cost of water; tap water $2 per 1000gal[vi]; produced water cost nothing for this work. Note that these costs are based on higher quality chemicals; savings could be realized using bulk fertilizers.

	F/2-Si			F/2-Si PW		
	g/L for F/2-Si	Cost per gram USD	Cost USD/1000L	g/L for F/2-Si	Cost per gram USD	Cost USD/1000L
NaNO3	3.75	0.0005	$1.88	0.749950309	0.0005	$0.38
CuSO4*5H2O	3.13E-05	0.33038	$0.02	0	0.33038	$0.00
FeCl	0.005322	0.734	$3.91	0.001	0.734	$0.74
NaH2PO4	0.152	0.001	$0.16	0.030399281	0.001	$0.04
ZnSO4	6.18E-05	0.2407	$0.02	0	0.2407	$0.00
MoO4	2.08E-05	0.572	$0.02	2.33E-06	0.572	$0.01
MnCl2	0.000411197	0.6037	$0.25	0.0000342	0.6037	$0.03
CoCl	1.98E-05	0.5423	$0.02	3.20E-06	0.5423	$0.01
Instant Ocean	38	0.0014	$53.20	21	0.0014	$29.40
Cost of water	1000	0.000529101	$0.53	1000	0	$0.00
Total Cost per 1000L			$60.01			$30.61

TABLE 1—Cost of $NaNO_3$ and NaH_2PO_4 were for industrial bulk[vii] while lesser used compounds were found at laboratory grade cost[viii]. This cost estimate yields a savings of 48.9918% of the cost of normally produced F/2-Si.

CONCLUSIONS

The high optical density data without a scaled amount of chlorophyll indicates there may be precipitate falling out of the produced water even after filtration. This would raise issue with how much light the algae are getting and thus inhibit growth more than in a solution made with fresh water. Another issue with precipitate forming is its effect on fuel quality. The PW treatment system should be refined at Eldorado Biofuels.

This experiment has shown that *NS 1776* has the ability to grow in F/2-Si media made with produced water. There is a longer period of lag before the algae beings to grow, however, *NS 1776* is not hindered completely. The rate of nitrate uptake is considerably slower using PW compared to FW. Also in comparison of PW to FW, there is not a swift spike in chlorophyll for PW from which we see at approximately cultivation day four in the FW. However, the algae does grow, although under stressed conditions. This stress is because of any number of conditions, such as the wrong species of a nutrient, bacterial contamination in the inoculants, precipitate forming which is absorbing the light, or possibly even a toxin from the treatment system. With further water treatment, the NS 1776 should be able to grow in a field setting. The lipid data was not available for this report; if higher lipid yields result from PW-induced stress, the lower growth may not be as important to overall biofuel production.

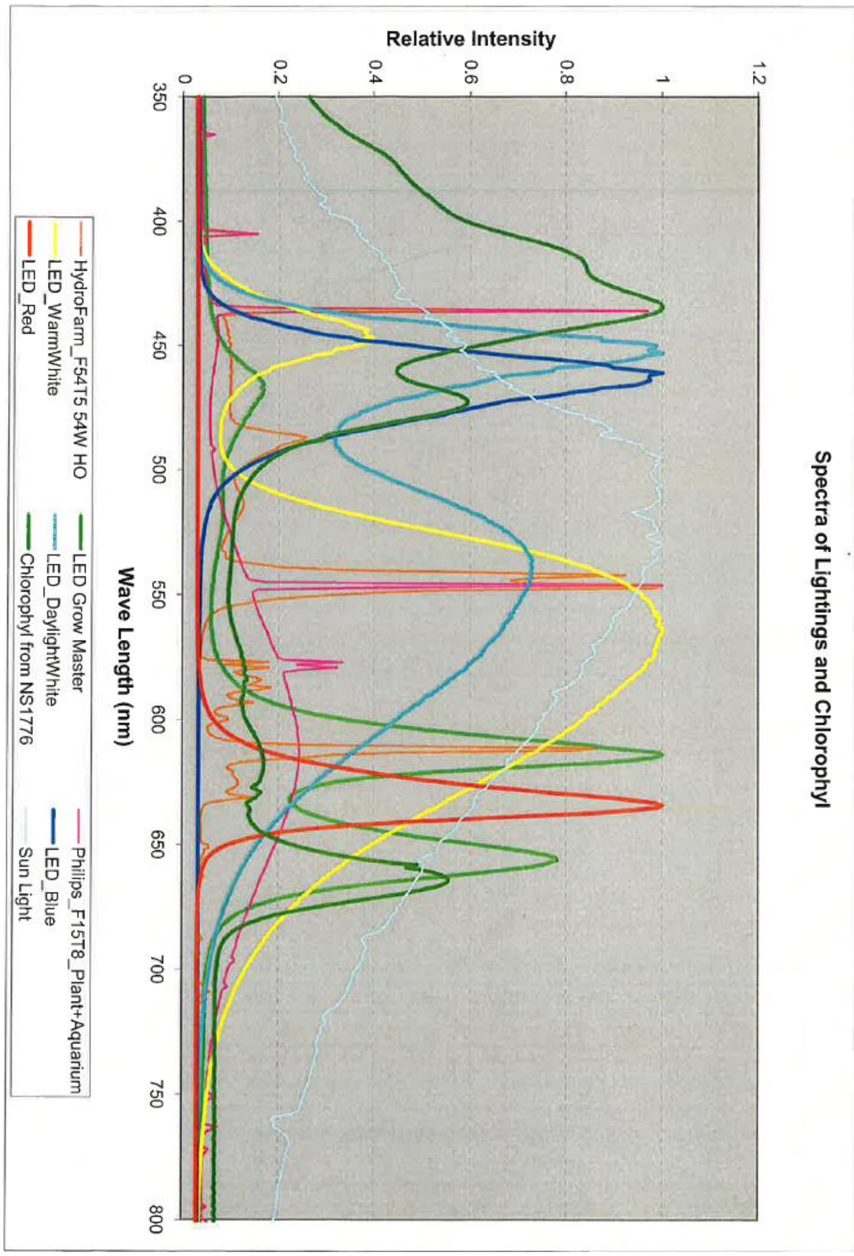
A cost analysis considering production of F/2-Si with produced and fresh water resulted in a savings of about one half the cost (44.38%) when using PW. Therefore, the product of this experiment is two directly proportional variables: cost and growth time; lower cost means shorter growth time, higher cost means higher growth time.

Produced water offers some major advantages to cost and water availability. There are also some drawbacks such as the chemistry which induces precipitation. Using produced water as a source for algal cultivation is nevertheless a topic which demands further research. Its successful development would open up regions thought to be too arid for responsible cultivation, provide oil and gas facilities with produced water disposal, and save algal cultivation facilities nearly half of the fertilizer costs.

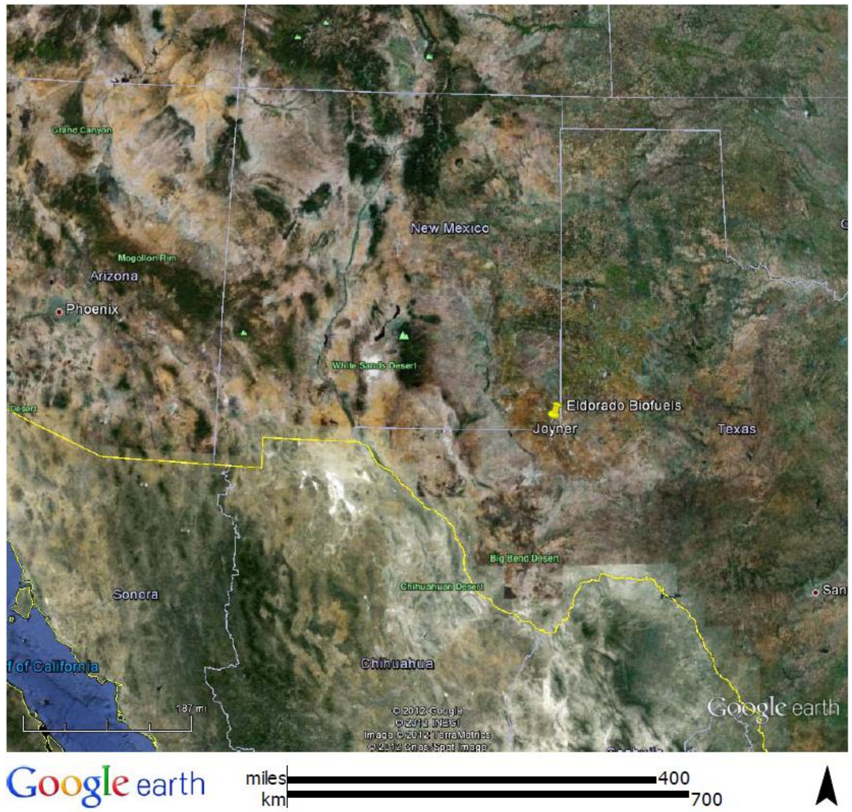
FUTURE WORK

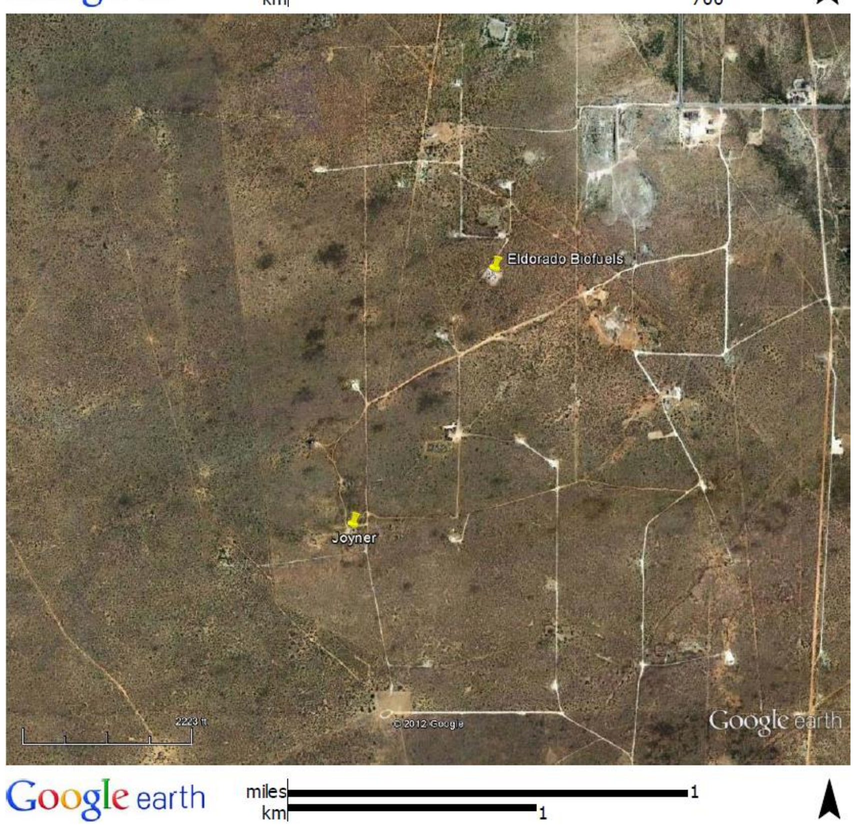
We are currently investigating alternative cost-effective water conservation methods and continuing our investigation into the complex water chemistry of treated produced well water.

APPENDIX A—PHILLIPS F15T8 LIGHT SPECTRUM



APPENDIX B—JOYNER WELL LOCATION


Grand Canyon
Mogollon Rim
Arizona
Phoenix
New Mexico
White Sands Desert
Eldorado Biofuels
Joyner
Texas
Big Bend Desert
Chihuahuan Desert
Sonora
Chihuahua
Google earth
miles
400
km
700


Eldorado Biofuels
Joyner
Google earth
miles
1
km
1

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[iv] Author witnessed.

[v] Ibid.

[vi] Drinking Water Costs and Federal Funding. EPA. 2004. http://water.epa.gov/lawsregs/guidance/sdwa/upload/2009_08_28_sdwa_fs_30ann_dwsrf_web.pdf

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[viii] Fischer Scientific. fischerscientific.com