

# Air Carbon for Algae Production (AirCAP) – Expanding algae resource potential via direct (in- pond) air-CO<sub>2</sub> capture

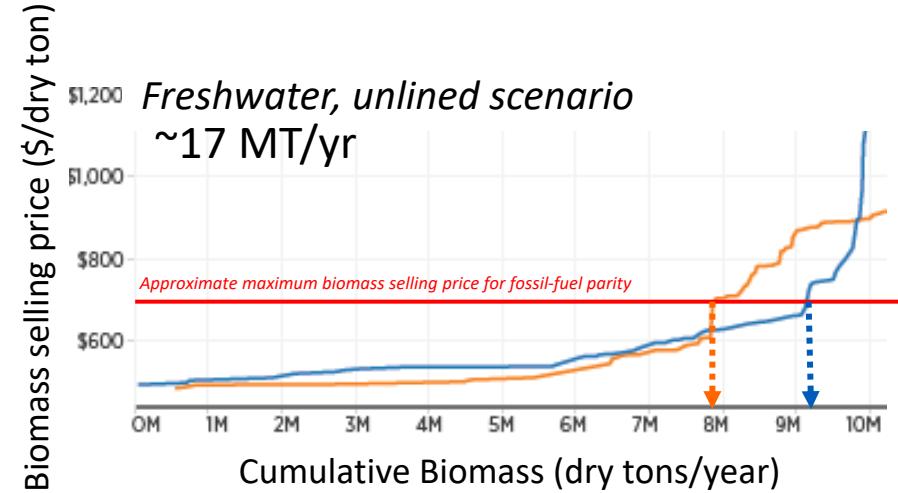
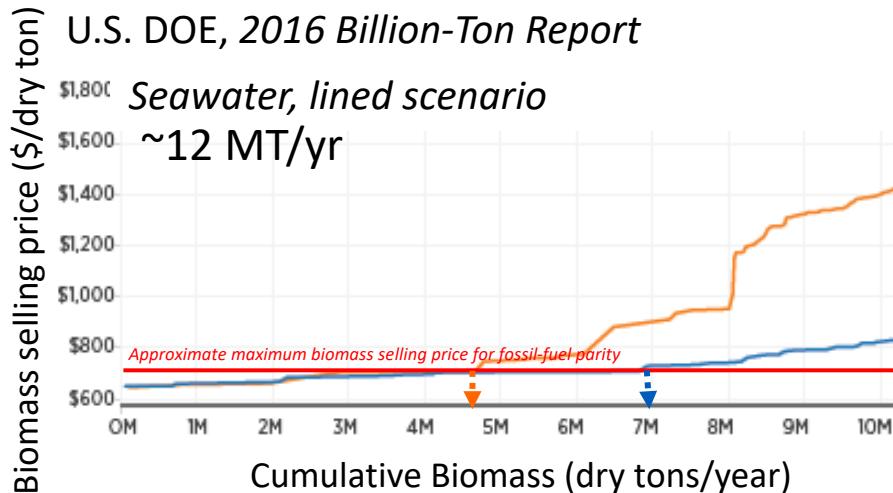
9<sup>th</sup> Annual International Conference on Algal Biomass, Biofuels and Bioproducts

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1. MicroBio Engineering Inc., 2. Pacific Northwest National Laboratory (PNNL), 3. Qualitas Health



# Why is direct air-carbon pond capture needed? Carbon supply via CO<sub>2</sub> co-location and bulk transport limits the resource potential of algal feedstocks



- Freshwater and saltwater cases yield ~30 MT/yr
- Sufficient for production of 2 – 5 billion gallons of gasoline equivalent per year, depending on conversion pathway

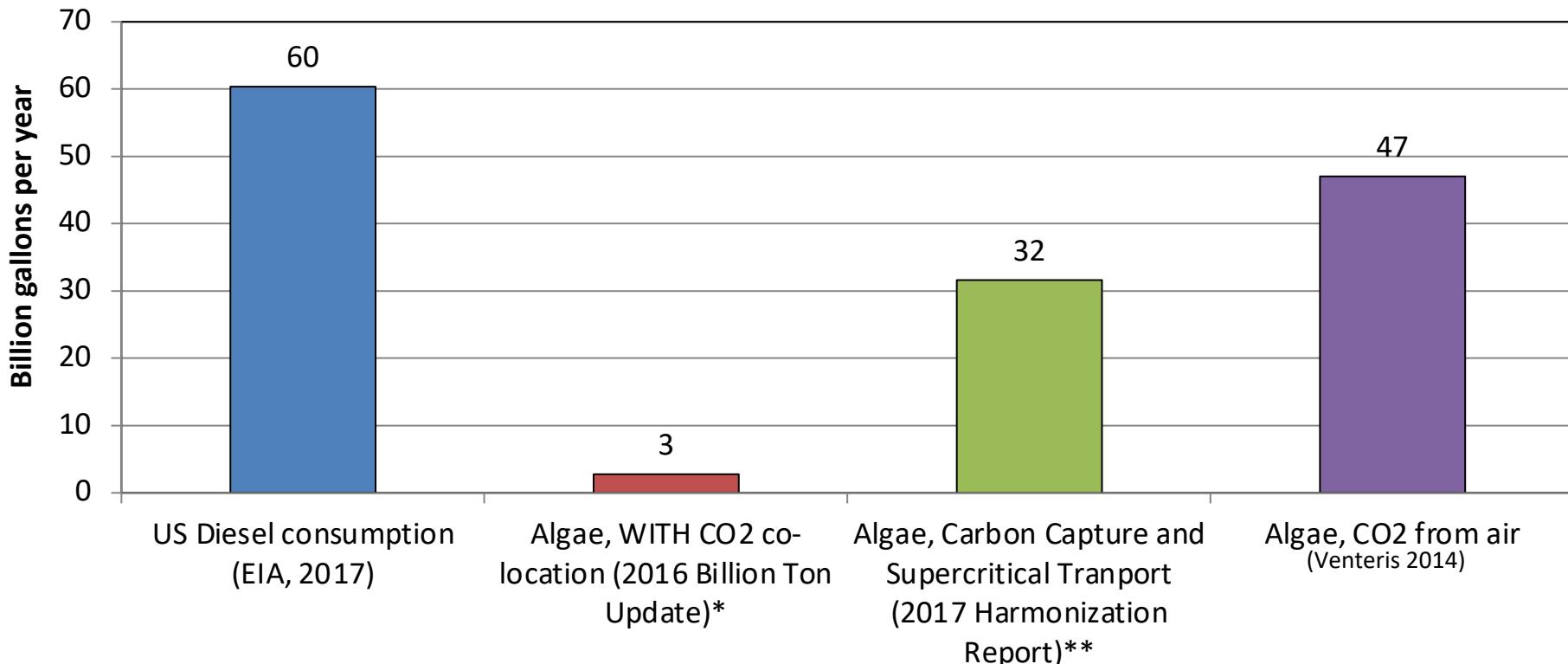
# 2017 Harmonization Report: Resource potential increases to ~340 MT/yr using 2<sup>nd</sup> generation carbon capture technologies and supercritical CO<sub>2</sub> transport



## Caveats:

- Carbon capture and CO<sub>2</sub> compression increase GHG emissions; paddle wheels must be turned off to meet the 50% GHG reduction relative to fossil fuels, or aggressive co-product strategies are required
- At this point, cost targets (~\$40/ton) have not been demonstrated at scale.

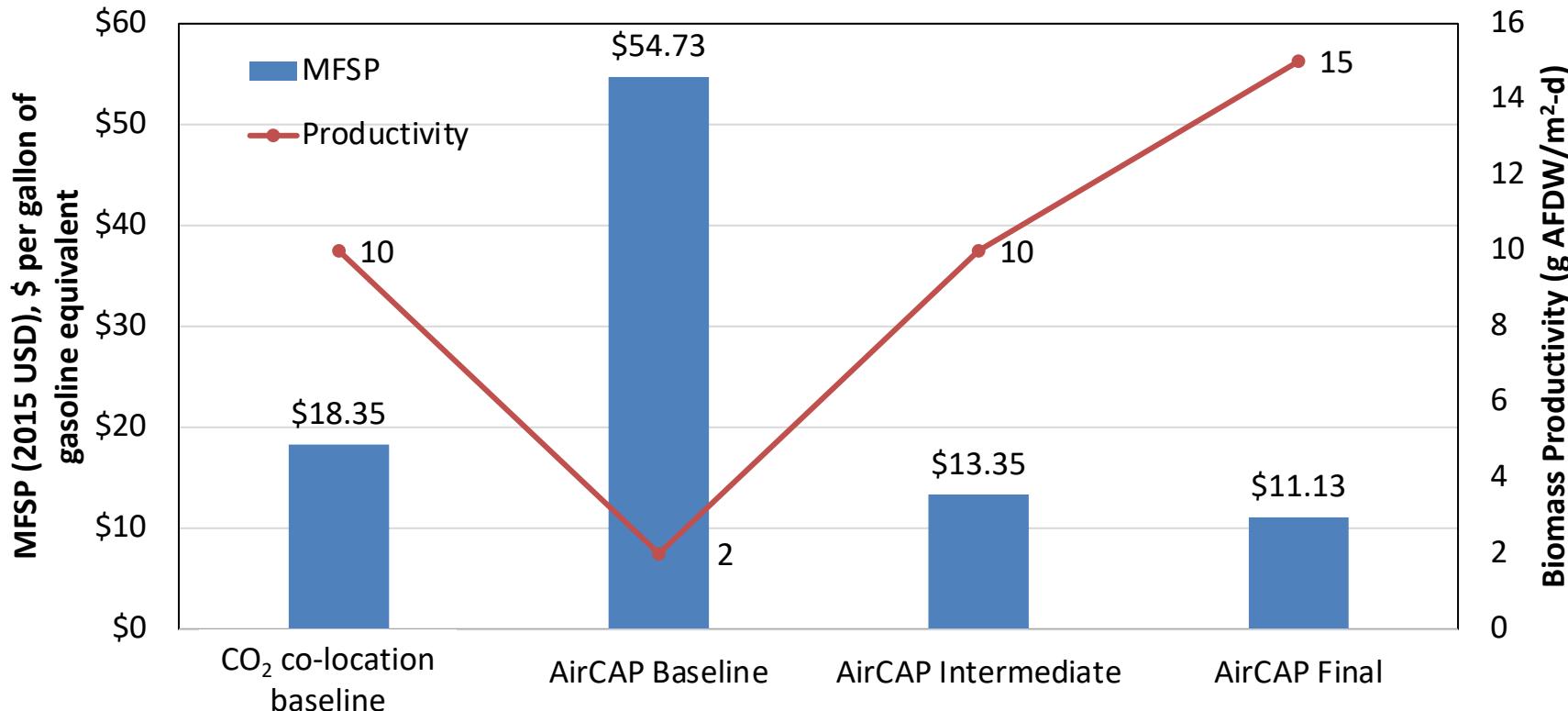
# Decoupling cultivation from CO<sub>2</sub> point-sources expands algal resource potential, and provides an alternative to the carbon capture/supercritical transport route



\*freshwater and saltwater scenario, present productivity. Assume 0.35 g diesel/gas per g of biomass.

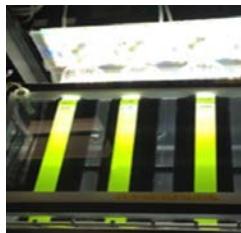
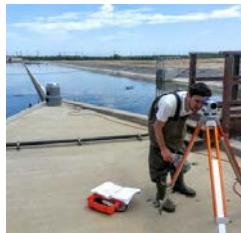
\*\*Assume 0.35 g diesel/gas per g of biomass (for comparison to the 2016 BTU case)

# MFSP parity to the co-location case only achieved if increases in biomass productivity are realized.

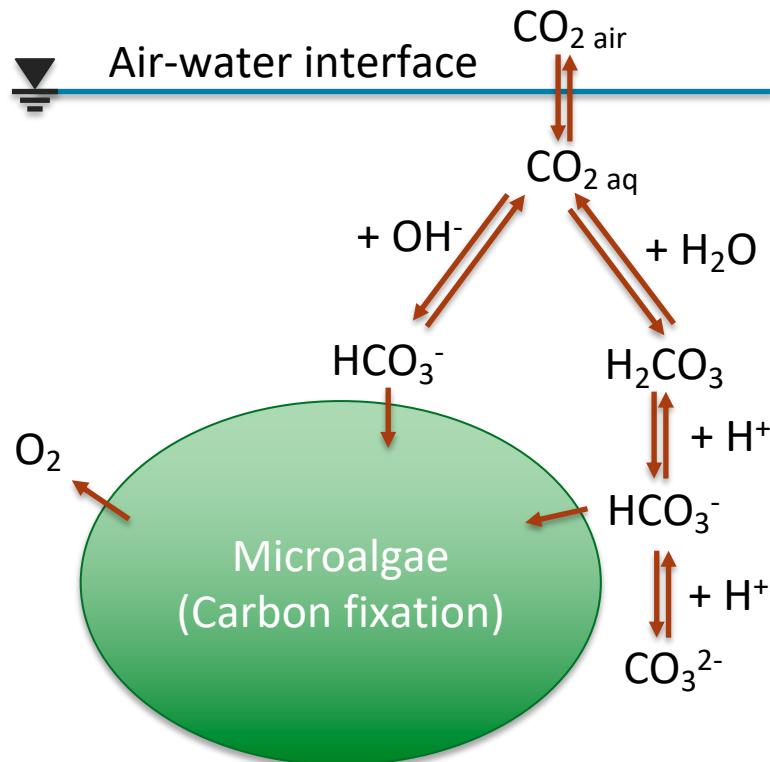


# Project Objective: Increase air-CO<sub>2</sub> mass transfer rates, and subsequently productivity using only air-CO<sub>2</sub>, via chemical enhancement (CO<sub>2</sub> + OH<sup>-</sup>)

- Identify the extent of chemical enhancement expected in pilot (4 m<sup>2</sup>) and demonstration (1-acre)
- Develop tools to predict mass transfer rates at pond sizes (10-acres) required for economies of scale
- Identify microalgae capable taking advantage of increased mass-transfer rates at high pH



# Background: Air-CO<sub>2</sub> mass transfer



Air-CO<sub>2</sub> flux ( $J_{CO_2}$ ) can be described by Fick's law:

$$J_{CO_2} = k_L^0 * \left( P_{CO_2}^{air} * H - C_{CO_2}^*(x = \delta) \right) * E$$

Where:

- "Piston velocity" (labeled under  $P_{CO_2}^{air} * H$ )
- "Driving force" (labeled under  $C_{CO_2}^*(x = \delta)$ )
- Enhancement factor (labeled under  $E$ )
- "Back pressure" (labeled under  $H$ )

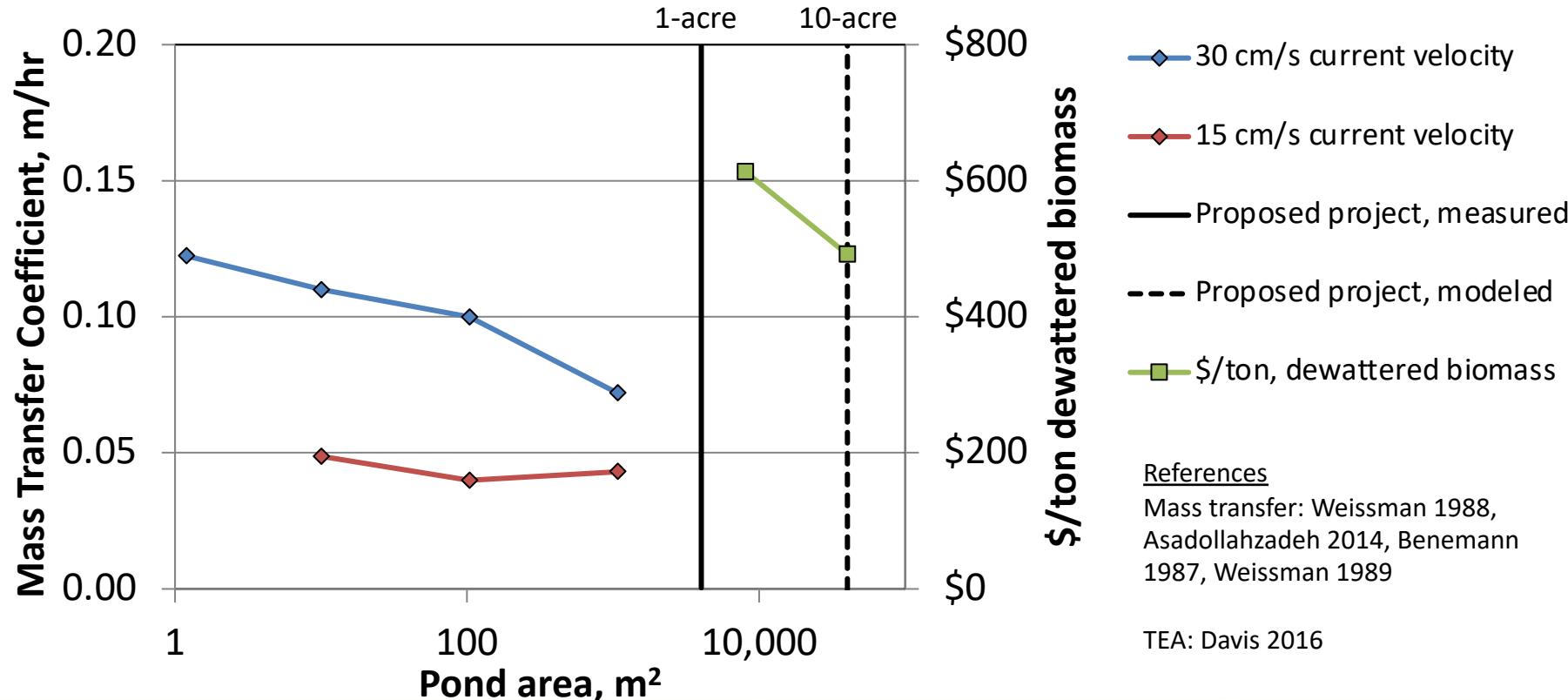
Where:  
 $k_L^0$  = mass transfer coefficient, m/hr, a function of pond hydraulics

$P_{CO_2}^{air} * H$  = Dissolved CO<sub>2</sub> concentration in equilibrium with air

$C_{CO_2}^*(x = \delta)$  = Dissolved CO<sub>2</sub> concentration some distance away from the air-water interface

$E$  = The extent of enhancement due to chemical enhancement (1 = no enhancement)

# The Transfer Coefficient, $k_L^0$ , approaches 0.05 m/hr at low current velocity and increasing pond size



# Simplifying assumptions lead to analytical expressions for chemically enhanced ( $\text{CO}_2 + \text{OH}^-$ ) mass transfer

Second order instantaneous reversible reaction, film theory  
(Danckwerts 1970, Olander 1960):

$$J_{\text{CO}_2} = k_L^0 * \left( P_{\text{CO}_2}^{\text{air}} * H - C_{\text{CO}_2}^*(x = \delta) \right) * \left[ 1 + \frac{D_{\text{OH}^-} \cdot D_{\text{HCO}_3^-} \cdot K \cdot [\text{OH}^-]}{D_{\text{CO}_2} (K \cdot C_{\text{CO}_2}^* \cdot D_{\text{HCO}_3^-} + D_{\text{OH}^-})} \right]$$

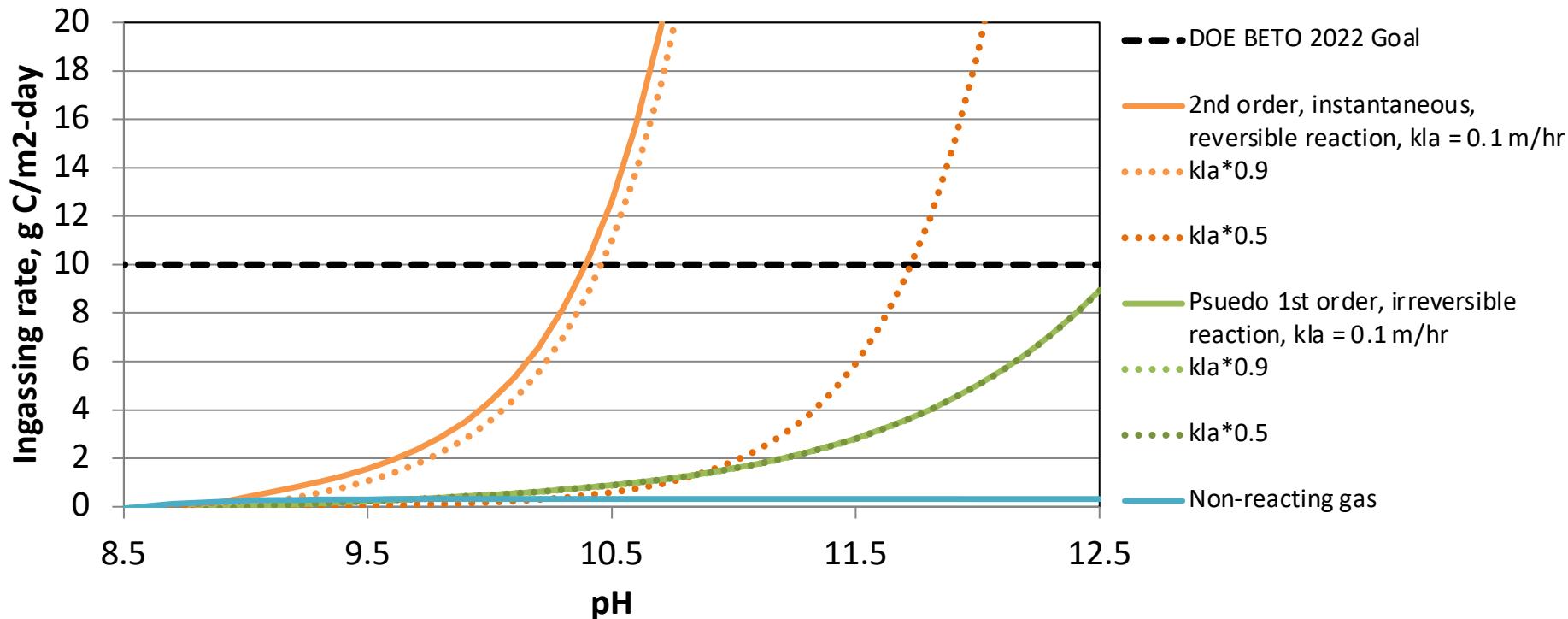
Driving Force

Enhancement factor

First-order irreversible reaction, film theory:

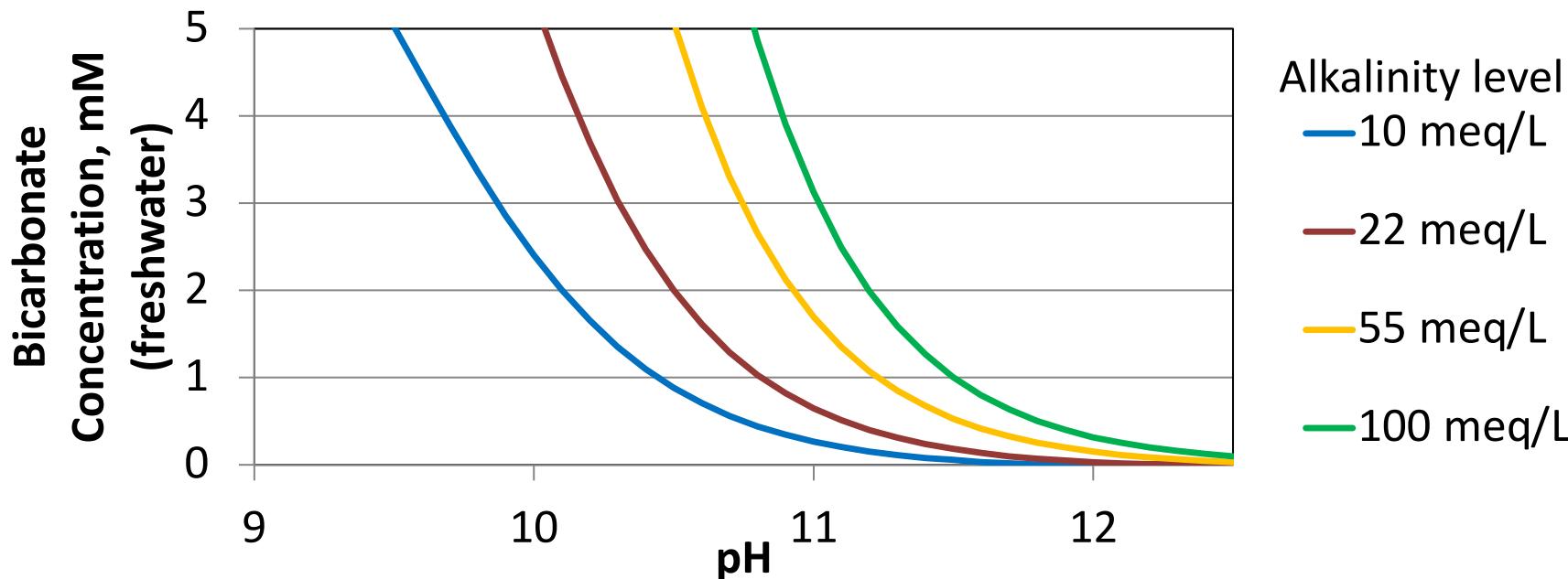
$$J_{\text{CO}_2} = \left( P_{\text{CO}_2}^{\text{air}} * H - C_{\text{CO}_2}^*(x = \delta) \right) * \left[ \sqrt{D_{\text{CO}_2} * k_{\text{tot}} * [\text{OH}^-]} * \coth \left( \sqrt{\frac{D_{\text{CO}_2} * k_{\text{tot}}}{(k_L^0)^2}} \right) \right]$$

# Predictions for the chemically enhanced ingassing rate vary significantly



Model response to  $k_L^0$  varies widely, leading to uncertainty regarding the effect of scale

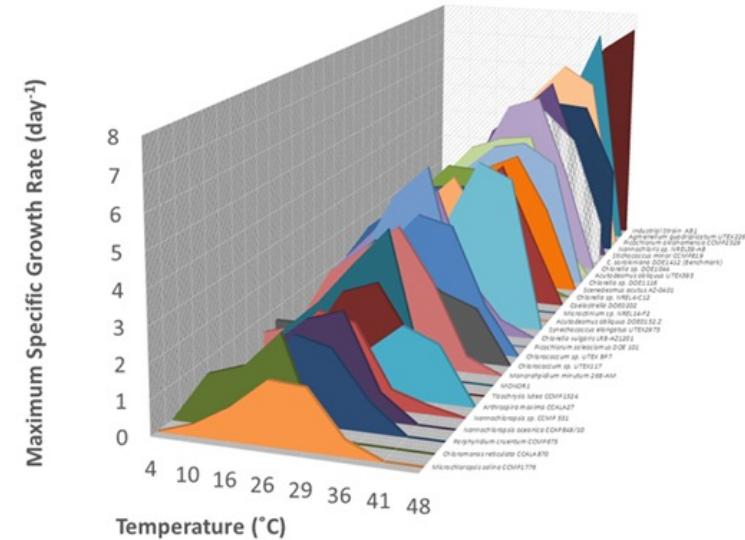
At high pH, supplemental alkalinity is required to maintain  $[\text{HCO}_3^-] > K_m$ , the half-saturation coefficient, although literature estimates vary by orders of magnitude (0.008 to 1.8 mM, Raven and Johnston 1991).



Additionally, source water containing Ca, Mg will likely precipitation at high pH, alkalinity, and may require pretreatment

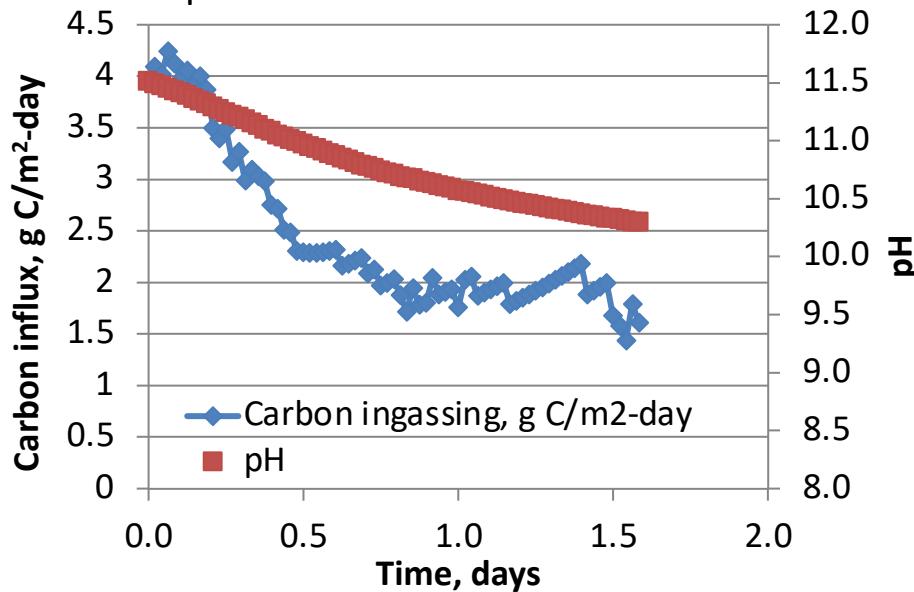
Unique organisms are required to withstand anticipated conditions (pH > 11) at which the air-CO<sub>2</sub> mass transfer rate is sufficient to support high biomass productivity

- Top DISCOVR strain, bioprospecting isolates to be screened for tolerance to high pH, under varying bicarbonate concentrations

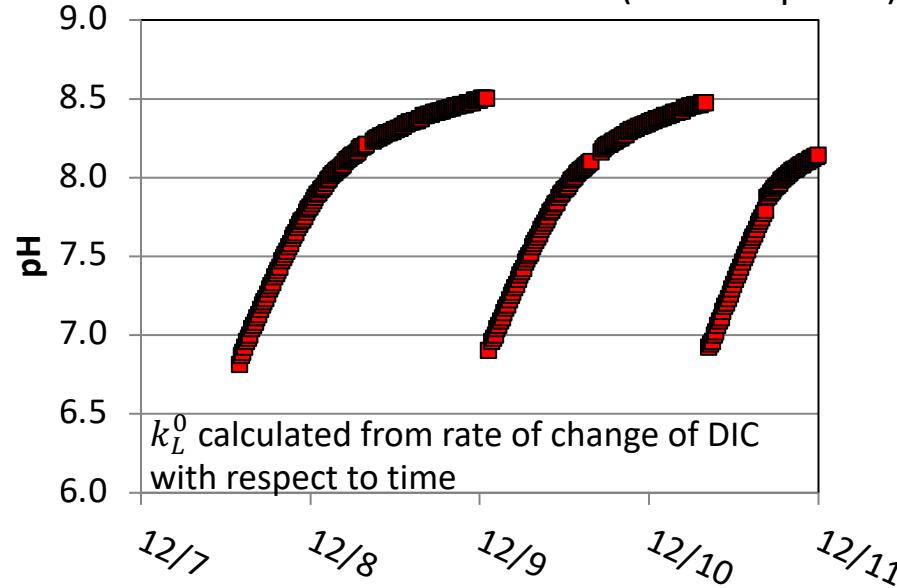


# Chemically enhanced ingassing rates will be verified in biotic and abiotic experiments

Ingassing experiments to confirm the model-predicted enhancement factor



Outgassing experiments to measure the transfer coefficient at demonstration scale (1.3 acre ponds)

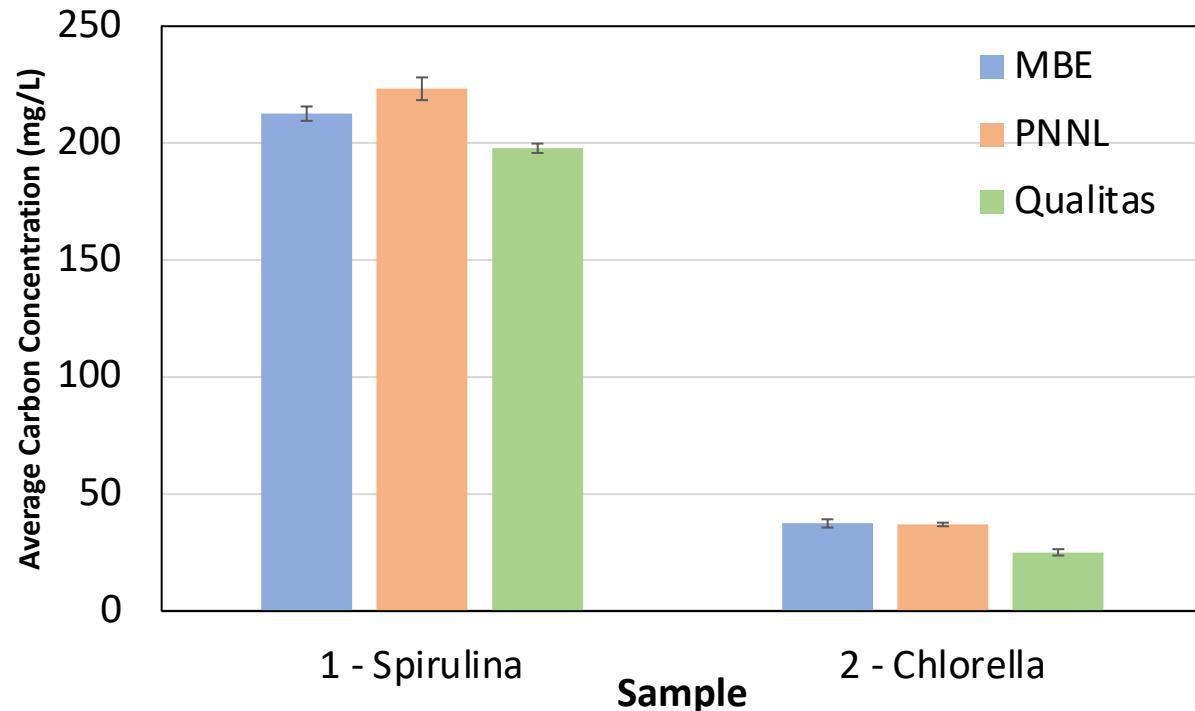


- Direct DIC measurements and flux cells (i.e. the rate of change of pCO<sub>2</sub>) to validate pH, alk calculations and equilibrium coefficients.

# An initial round robin aligned analytical methods between project partners to allow accurate and reproducible carbon mass balances

Input parameters:

- pH
- Salinity
- Alkalinity
- Dissolved inorganic carbon (by NDIR)
- Dissolved organic carbon (as NPOC)
- Particulate inorganic carbon (by CHN, combustion)
- Particulate organic carbon (by CHN, combustion)
- Ingassing rate (from experiments or models)



# Conclusions

- Point-source CO<sub>2</sub> co-location limits algal resource potential
- 2<sup>nd</sup> generation carbon capture technologies, combined with supercritical CO<sub>2</sub> transport, have the potential to greatly expand resource potential, but aren't yet proven
- Capturing CO<sub>2</sub> from the air is a possible alternative, but requires harsh (high pH conditions)
- Strain screening is required to identify appropriate strains
- Abiotic and biotic experiments, in-silico and at scale, will determine technology feasibility

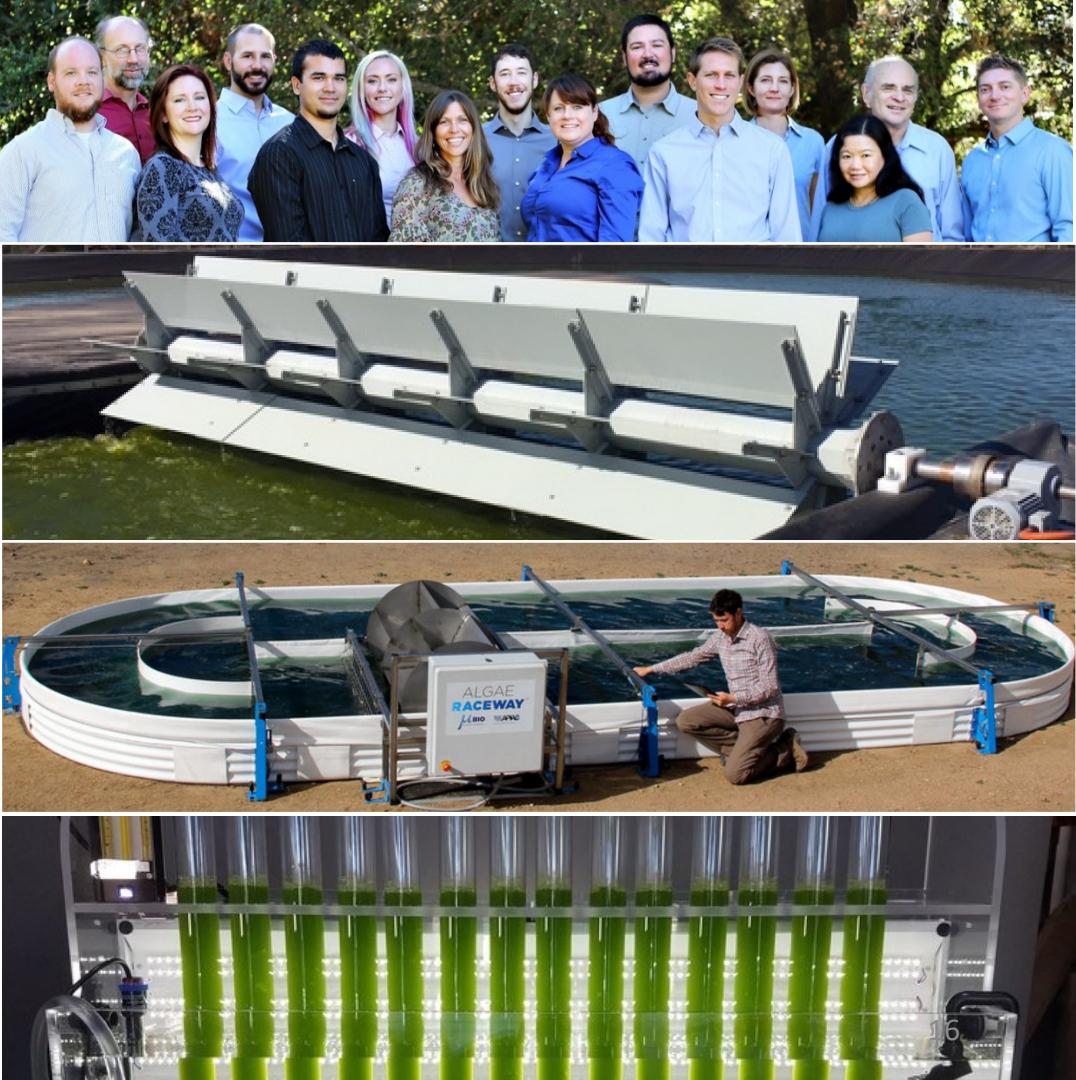
# Acknowledgements

- Support from DOE-BETO, Enhancing Carbon Utilization in Algal Systems FOA





- Facility Designs
- Algae Equipment
- Research and Development
- Business Consulting
- Techno-Economic Analyses
- Life Cycle Assessments



# Introducing the Bubble Column Array

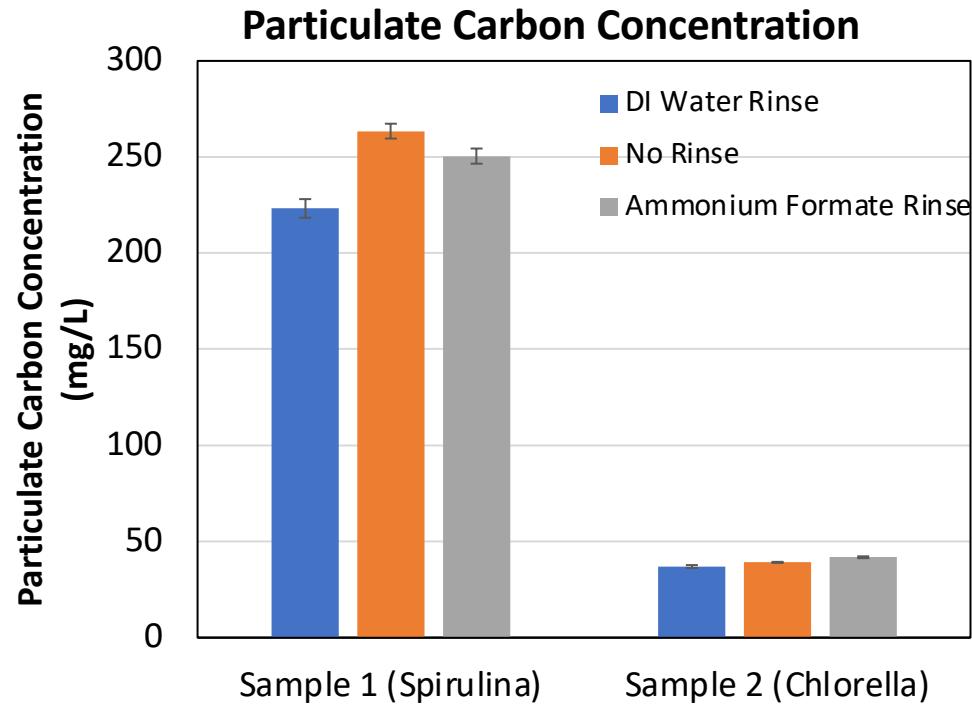
- 14 PBRs in one
- Best value per PBR unit
- Programmable temperature
- Programmable LEDs up to 1680  $\mu\text{mol}/\text{m}^2\text{-sec}$
- Proven to resist contamination
- Increased throughput



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Subtle variations in analytical methods (i.e. rinsing volume, rinse composition) in AFDW, particulate organic carbon determination can confound the carbon mass balance



# In mass-transfer model, Fick's 2<sup>nd</sup> law to be solved numerically to yield predictions of the air-CO<sub>2</sub> flux.

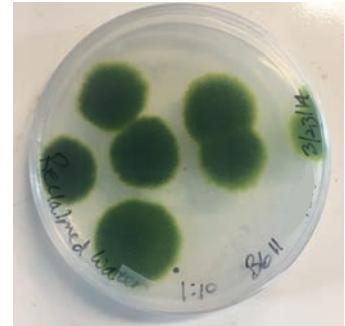
$$\frac{\partial c_A(x, t)}{\partial t} = D_A \frac{\partial^2 c_A(x, t)}{\partial x^2} - z_A D_A \frac{F}{RT} \frac{\partial(\phi(x, t)c_A(x, t))}{\partial x} + r_A(x, t).$$

- One initial condition, two boundary conditions (for each component) required.
- Stiff numerical solver (i.e. Matlab ODE15) required
- Nernst-Einstein equation:  
$$\phi(x, t) = \frac{RT}{F} \frac{\sum_{q=1}^{NC} z_q D_q \frac{\partial c_q(x, t)}{\partial x}}{\sum_{q=1}^{NC} z_q^2 D_q c_q(x, t)}$$
- Accounts for diffusion due to differences in local ionic charge
- Reaction term:  
$$CO_2 + OH^- \xrightleftharpoons[k_{12}]{k_{11}} HCO_3^-$$
$$HCO_3^- + OH^- \xrightleftharpoons[k_{22}]{k_{21}} CO_3^{2-} + H_2O$$
$$OH^- + H^+ \xrightleftharpoons[k_{32}]{k_{31}} H_2O$$
$$CO_2 + H_2O \xrightleftharpoons[k_{42}]{k_{41}} HCO_3^- + H^+$$

The mass-transfer model will be validated with experimental results from Task 3.

# Bioprospecting for alkaliphilic strains

- Obtain inoculum from high pH environments (possible locations: Soap Lake, Soda Lake, Mono Lake, Searles Lake, Walker Lake, Owen's Lake)



Left: [http://www.ifiberone.com/news/soap-lake-approves-mineral-water-use-for-future-manufacturing-plant/article\\_26852ebc-c0a3-11e5-8ca7-4767f5189d09.html](http://www.ifiberone.com/news/soap-lake-approves-mineral-water-use-for-future-manufacturing-plant/article_26852ebc-c0a3-11e5-8ca7-4767f5189d09.html)  
Right: <https://www.atlasobscura.com/places/searles-lake>

- Obtain isolates using plating or FACS approaches

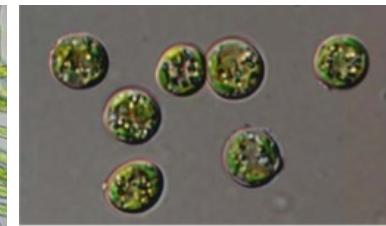
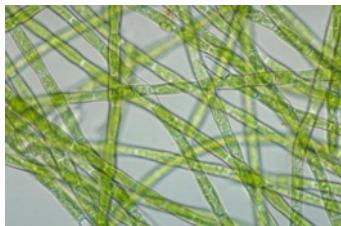
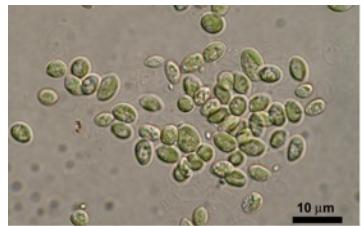
What bioprospecting techniques will be used to identify alkaliphilic strains for further evaluation? Will techniques differ for eukaryotes and prokaryotes? (Media composition, scale, number of organisms, etc.)

# Bioprospecting for alkaliphilic strains

- Isolates that perform well in high pH and alkalinity will be characterized (physiological and molecular studies)



- Particular chemicals can be applied that select for yellow-green algae in the Kingdom Chromista (including Eustigmatophytes, Xanthophytes, Bacillariophytes) as opposed to Chlorophytes.





# Acknowledgment

This work is supported by the U.S Department of Energy (DOE):  
Bioenergy Technologies Office (BETO).

“AIR CARBON FOR ALGAE PRODUCTION - AIRCAP.”, DE-EE0008519, 2018-2022.

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