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## Motivation

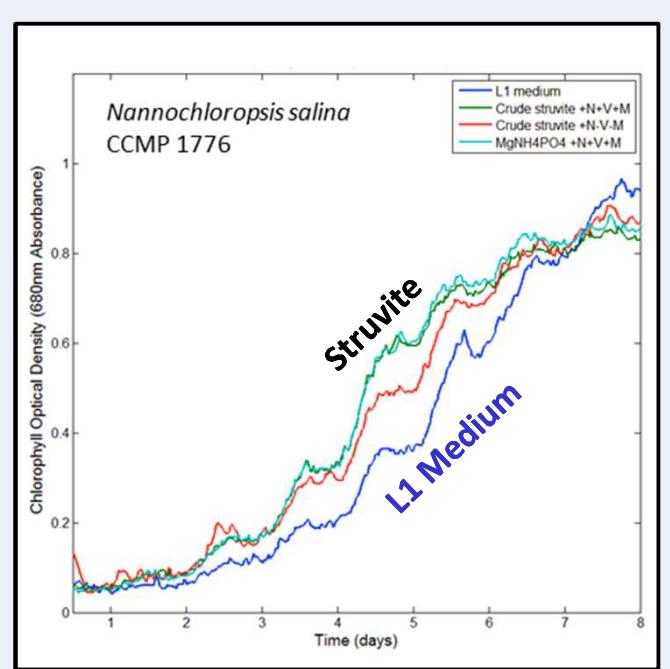
In order to replace 10% of liquid fuels with algae based fuels (roughly 30 BGY), the required amount of phosphorous required for algae production would be 2.6-6 Mt/yr. In 2006, worldwide production of phosphorous was around 4.1 Mt/yr<sup>1</sup>. Further, the algae production would also require more nitrogen than was produced in 2006. Recent life cycle analyses have also pointed out the high costs of nutrients. Further, to be feasible, nutrient use for algae production should not compete with food production. If algae based biofuels are to be economically competitive, an efficient, effective method of nutrient recycling must be developed.

Here, we present our work examining struvite ( $MgNH_4PO_4$ ) as a potential nutrient source for algae cultures and propose a process by which phosphate and nitrogen can be remineralized and precipitated as struvite to be returned to the algae culture. Conditions affecting the precipitation behavior of struvite as well as the resulting particle size distributions are measured. Efforts at modeling precipitation behavior are also presented.

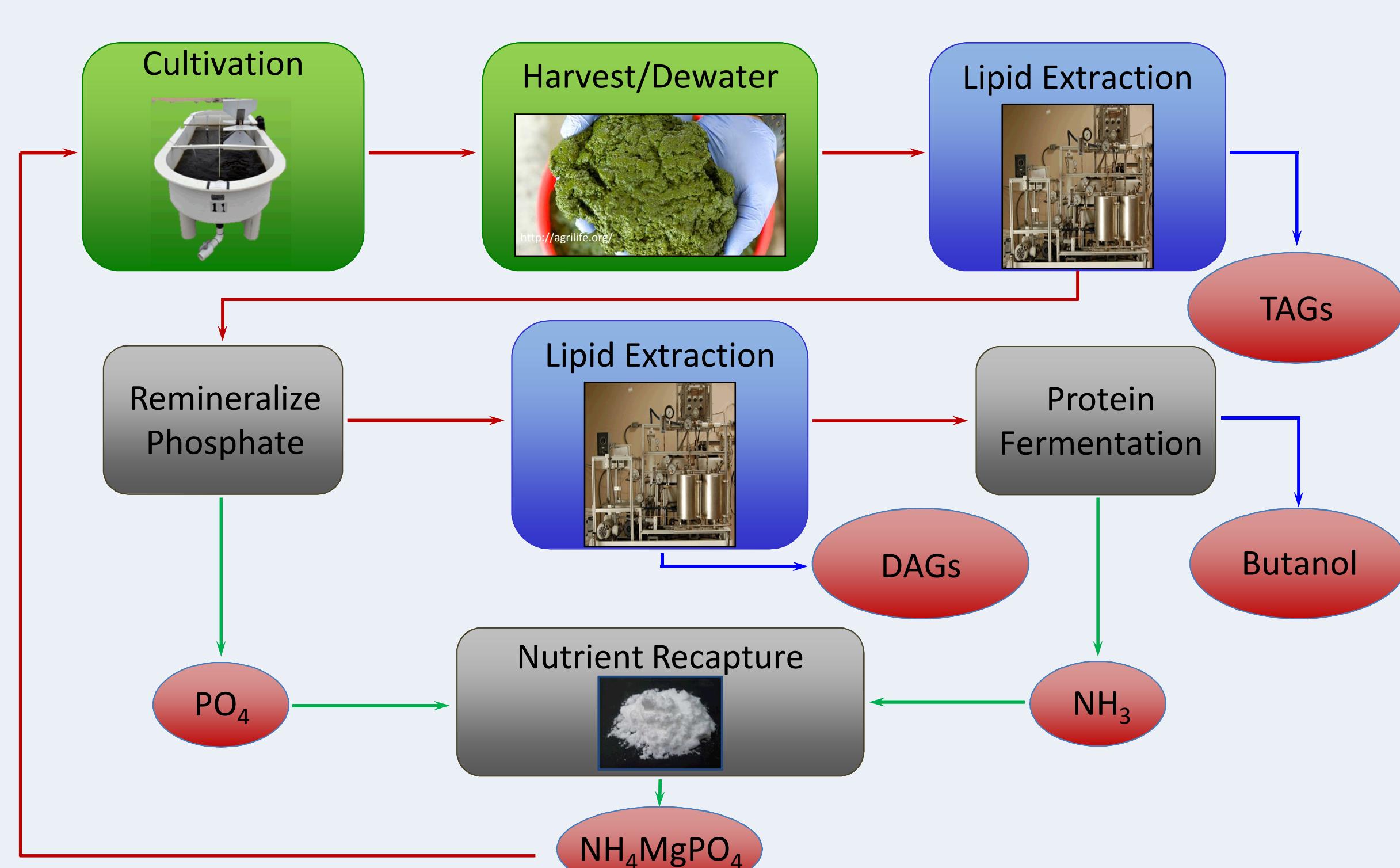
<sup>1</sup>Pate et al., *Applied Energy* 88(2011)377-3388

## Why Struvite?

Convenient and transportable (solid)  
Recovers 1:1 N:P  
Precipitates at accessible concentrations and pH ranges  
Involves Mg readily available in seawater  
Experience in wastewater treatment industry

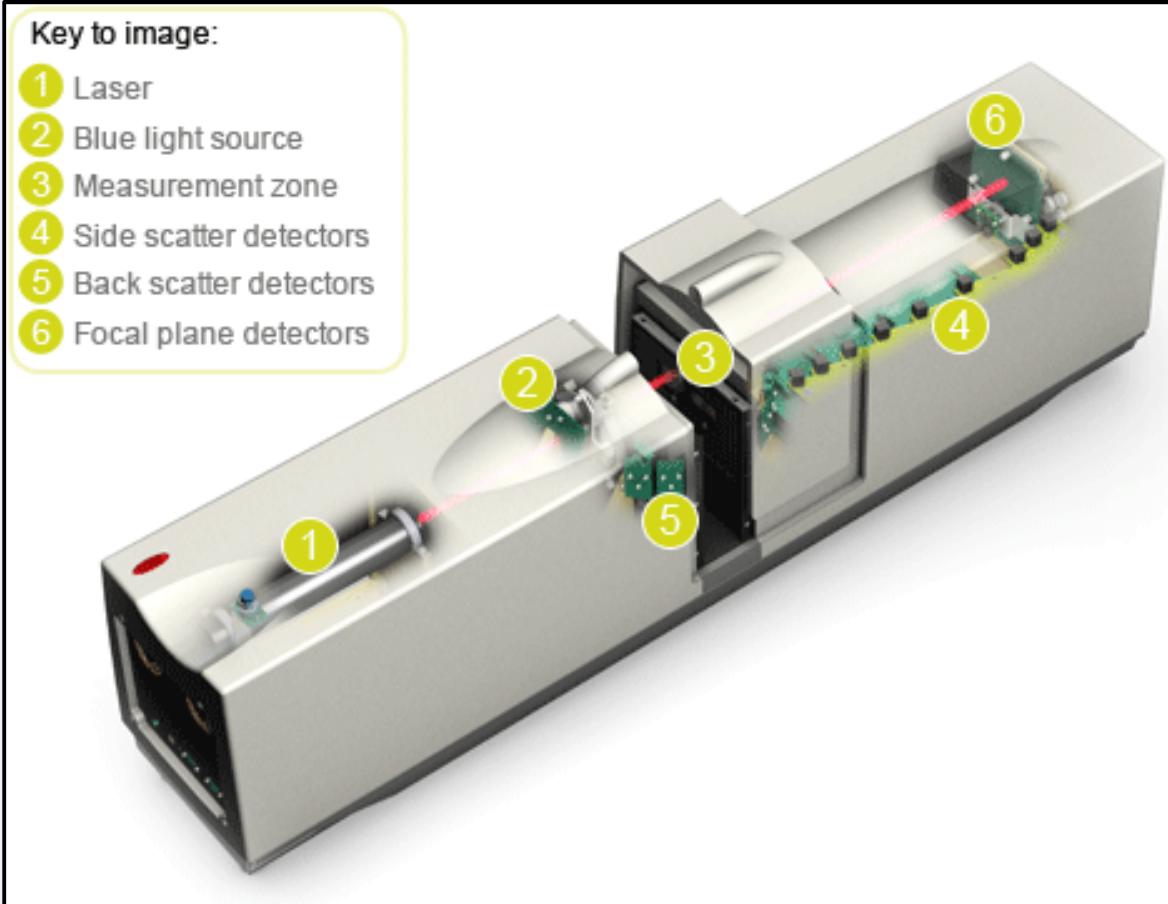


## Proposed Process

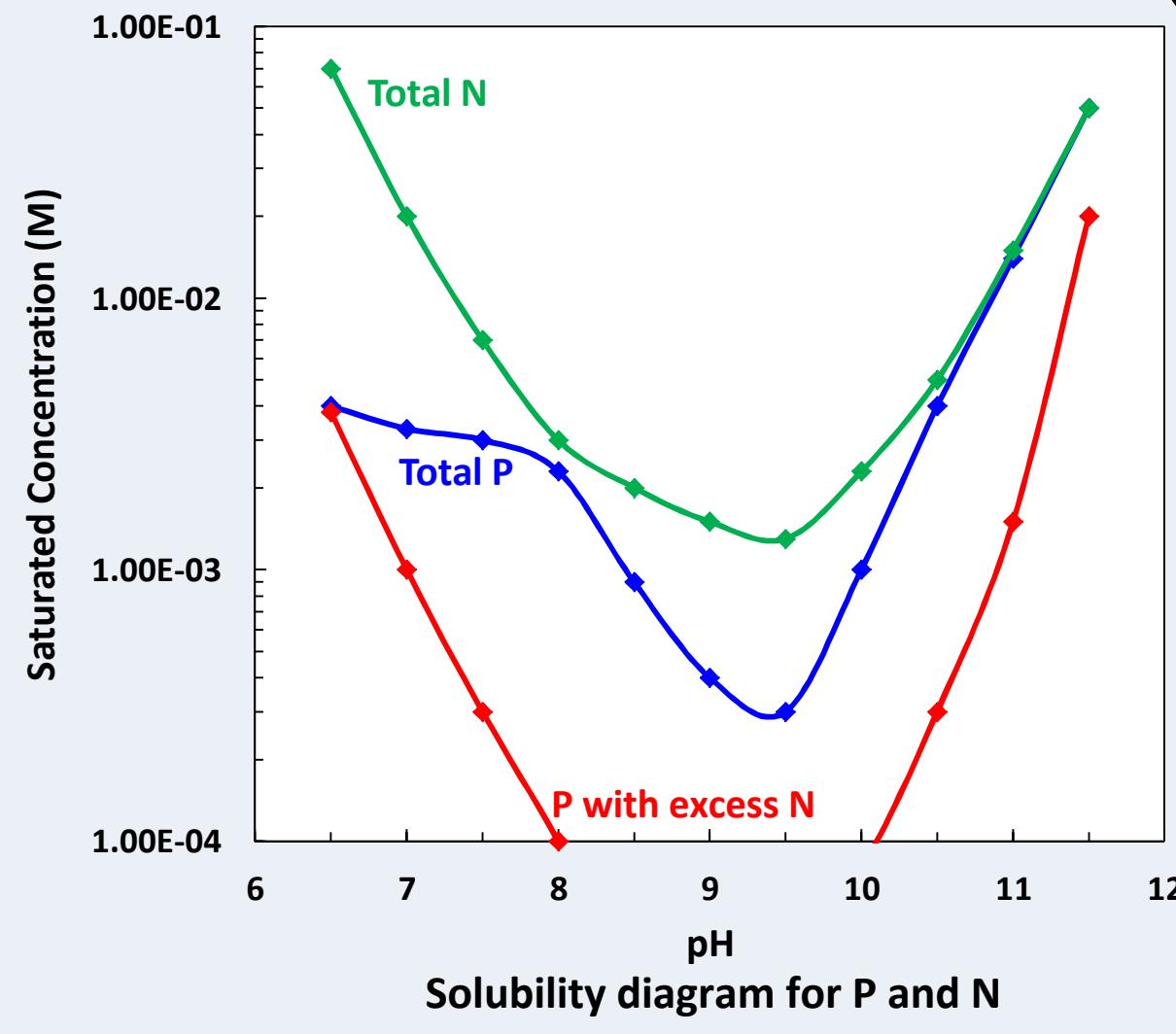


## Struvite Precipitation

### Precipitation Measurement

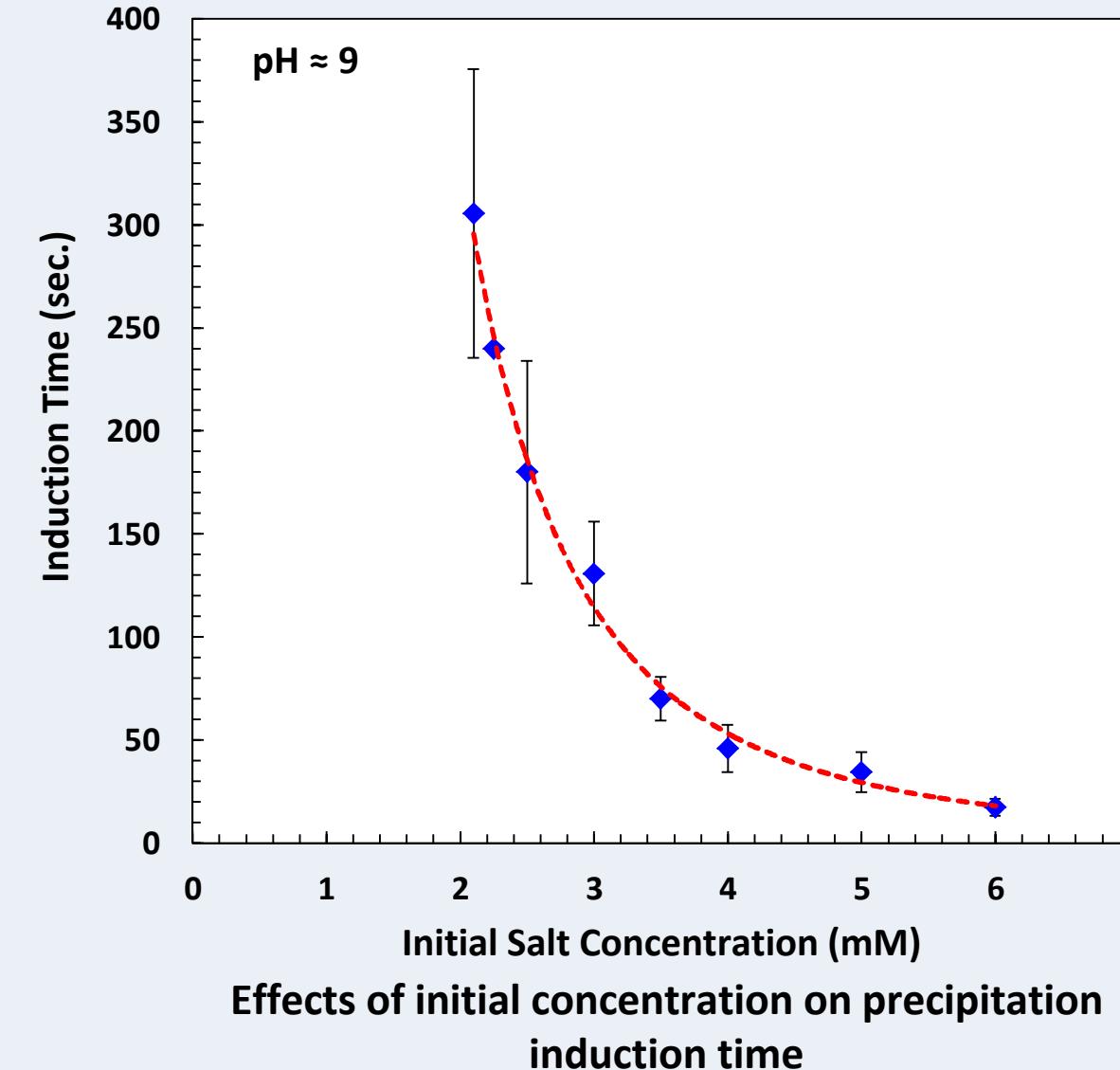


Precipitation measurements made in situ using laser diffraction (Malvern Mastersizer 2000)  
Gives size distributions (volumetric), distribution moments, particle statistics  
Sample handler allows mixing speeds of 1000 – 3000 rpm  
Struvite most likely to precipitate when solubility of P in and excess of N is at a minimum  
Based on solubility data (at right), all experiments conducted at pH 8.5 – 9.0 (reasonable for algae applications)  
Minimize constituent solubility = maximize precipitation

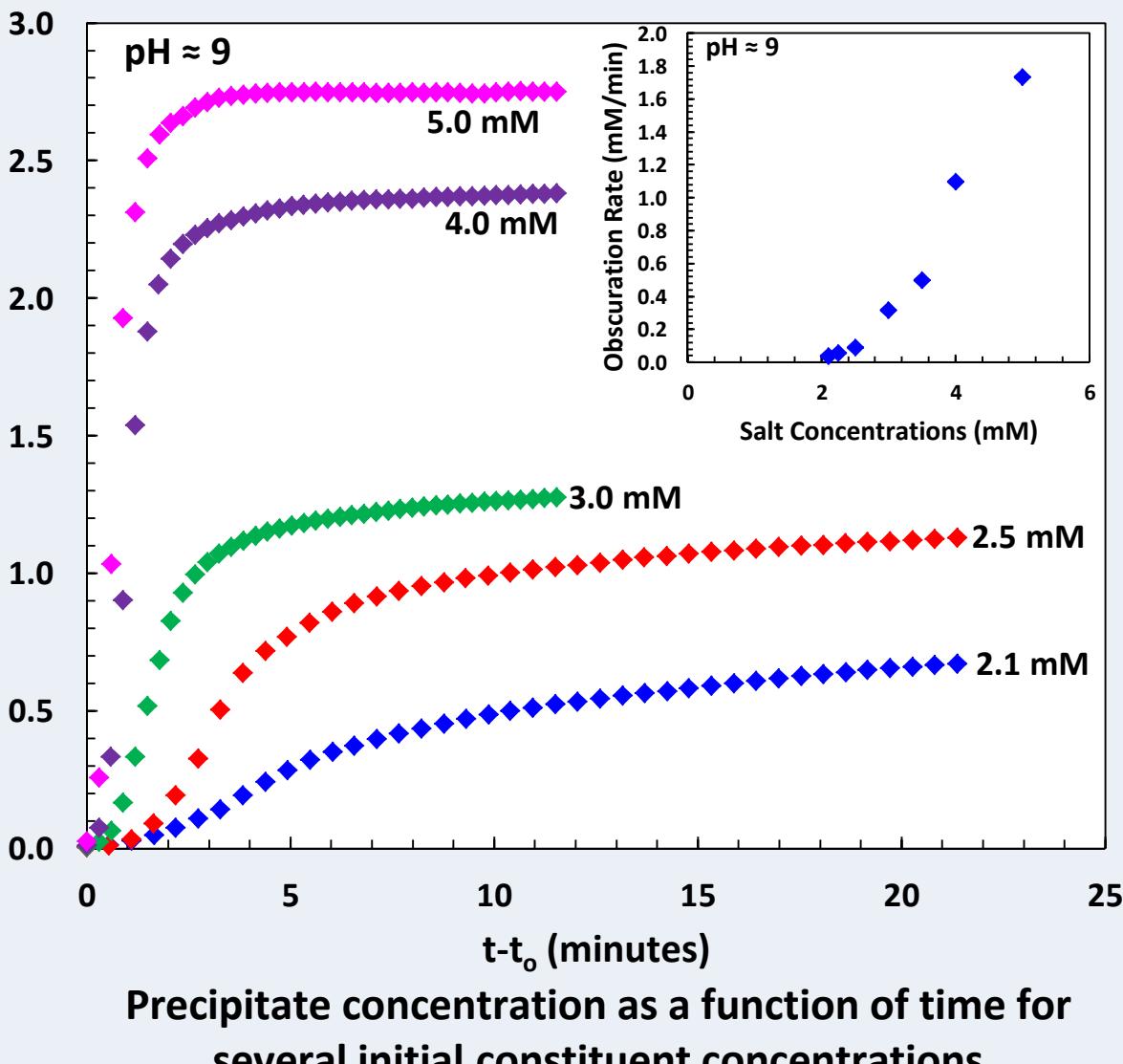


### Particle Growth

Induction time – time required for precipitation to begin at pH > 8.5  
Induction time decreases exponentially with increasing supersaturation (concentration)  
Below supersaturation conditions, precipitation does not occur  
At sufficiently high supersaturation, precipitation occurs immediately

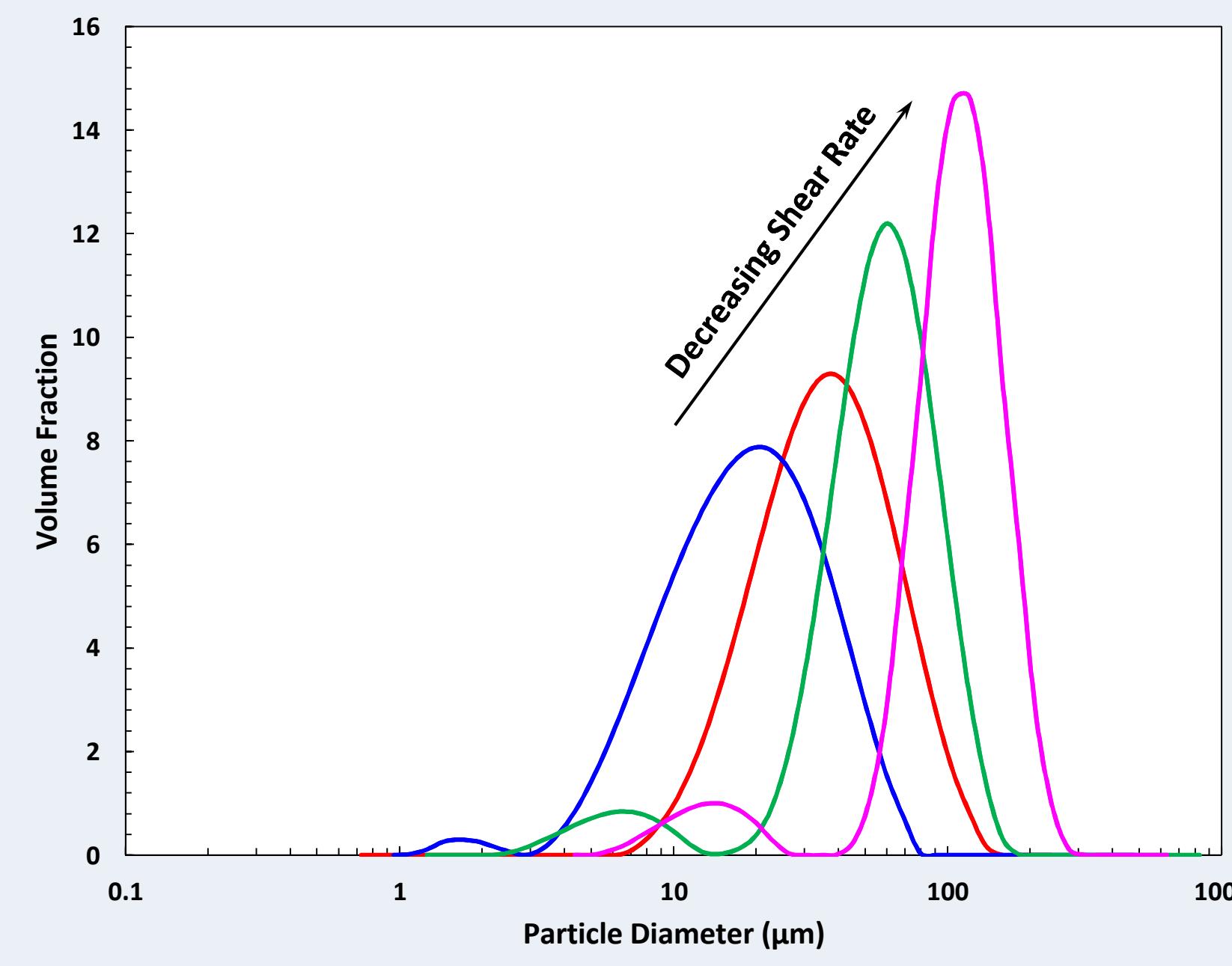


Mass of struvite precipitated depends strongly on the initial constituent concentrations  
Strongest dependence observed at highest supersaturations  
Higher supersaturation produces more precipitate  
Precipitation rate (initial slope) also strongly dependent on supersaturation  
High supersaturation produces faster precipitation rates



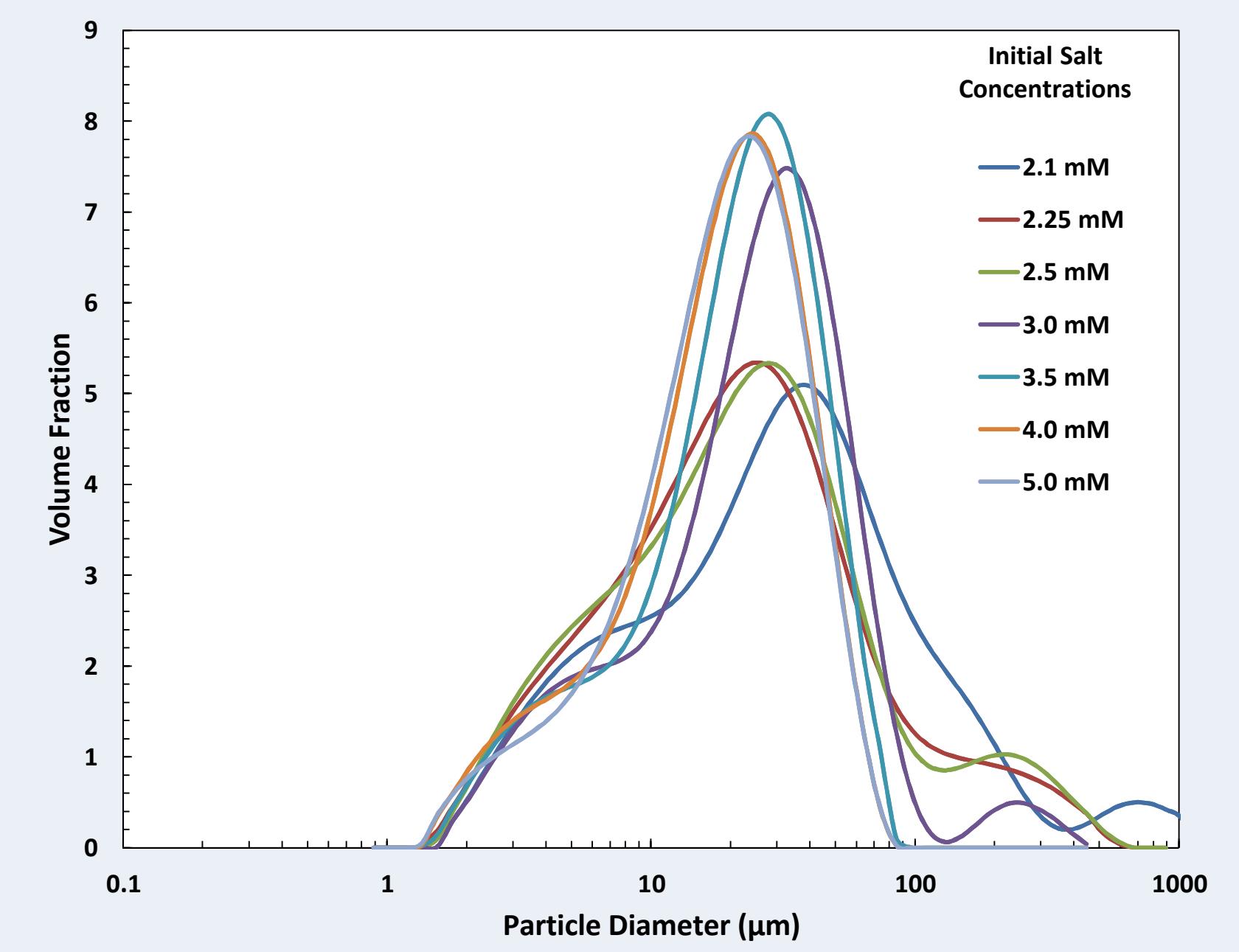
### Equilibrium Distributions

Shear rate has a significant effect on the equilibrium particle size  
High shear rates produce smaller, more broadly distributed particles  
Shear stress in these flows causes larger particles to break up  
Low shear rates results in larger (order of magnitude) particles that are more uniformly distributed  
Lower shear stress enables larger particles to hold together



Effects of shear rate on the equilibrium particle size distributions

Supersaturation also effects the equilibrium particle size distribution  
Low supersaturation results in broadly distributed particles sizes  
Particle growth is more favorable than nucleation  
High supersaturation produces more narrowly distributed particles  
Particle growth and nucleation of new particles is more balanced under these conditions



## Precipitation Modeling Approach

### Evolve the distribution moments

$$\frac{dN}{dt} = \dot{N} = k_{nuc} \exp\left(-\frac{B_{nuc}}{SI^2}\right)$$

$$\frac{dM_n}{dt} = \dot{N}m_0 + k_s a_A \text{sign}(\sigma) |\sigma|^b M_{\frac{n}{3}}$$

4 Parameters

$$M_{\frac{2}{3}} = N^{\frac{1}{3}} M_1^{\frac{2}{3}} \quad M_{\frac{5}{3}} = M_1^{\frac{1}{3}} M_2^{\frac{2}{3}}$$

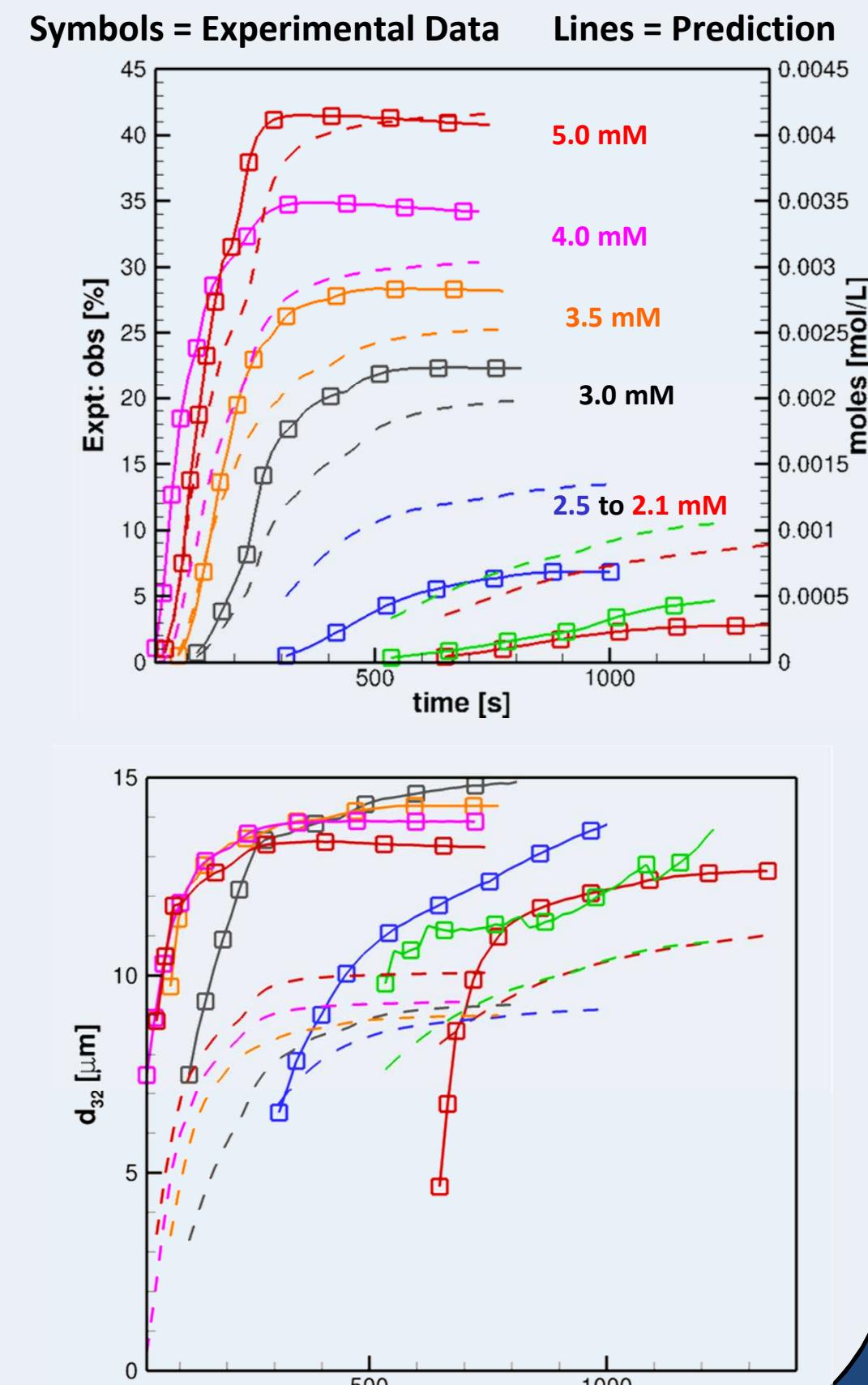
Intermediate moments obtained via logarithmic Lagrange interpolation

## Model Results

Qualitative agreement between measured obscuration and predicted mass precipitated

Some discrepancies in the “calibration factor” between obscuration and mass concentration

Larger adjustment needed for intermediate concentrations while a smaller correction needed for low concentrations



Related more to model form than parameters chosen

## Conclusions

- Processes for recycling algae nutrients in the form of struvite are being developed
- Algae have been successfully cultivated using struvite as nutrient source
- Struvite precipitation kinetics in a well controlled conditions have been studied
  - Size distributions, induction time, kinetics all strongly depend on supersaturation conditions
- Generally reasonable modeling results
  - Thermodynamics must be addressed for improvement
  - Mixing effects may need to be included

## Future Work

Based on work by Kofina et al.<sup>2</sup>, added organic materials likely to be found in the algae extract are likely to negatively impact struvite precipitation

Quantifying and developing models capable of predicting these effects is ongoing

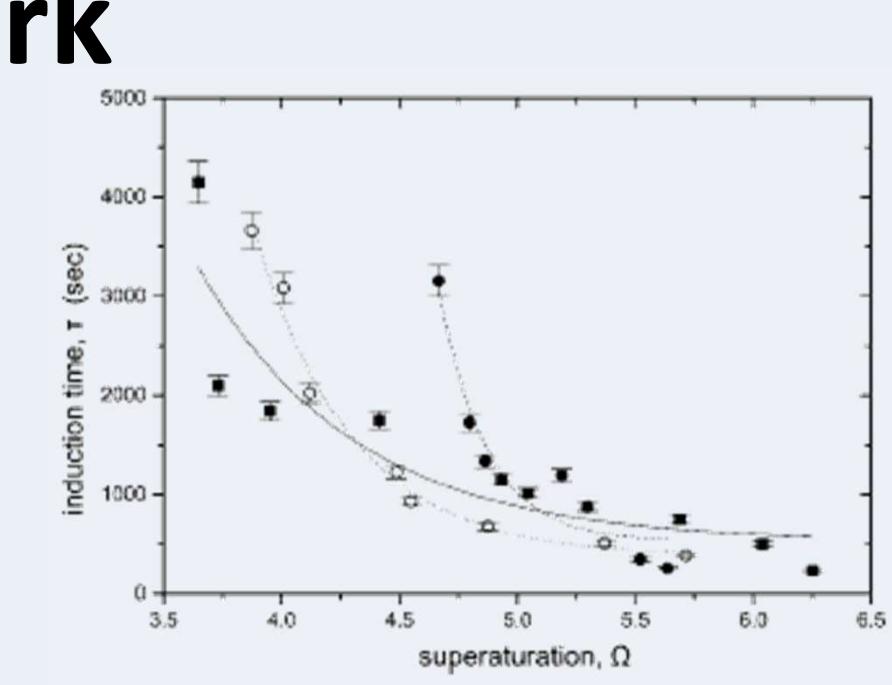


Figure 1. Stability diagram for struvite in synthetic wastewater. In the absence of additive (■), in the presence of 1 μM citrate (●), and in the presence of 1 μM phosphocitrate (○).

<sup>2</sup>Kofina et al., *Crystal Growth and Design*, 7(2007)2705-2712