# Conceptual Model of Ammonium Utilization at the Base of the Delta Food Web

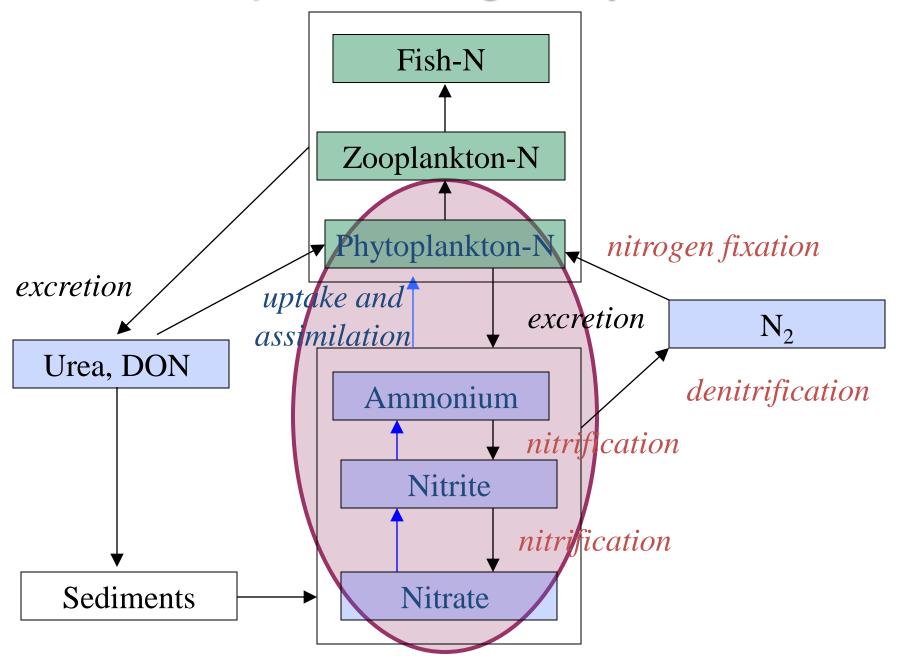
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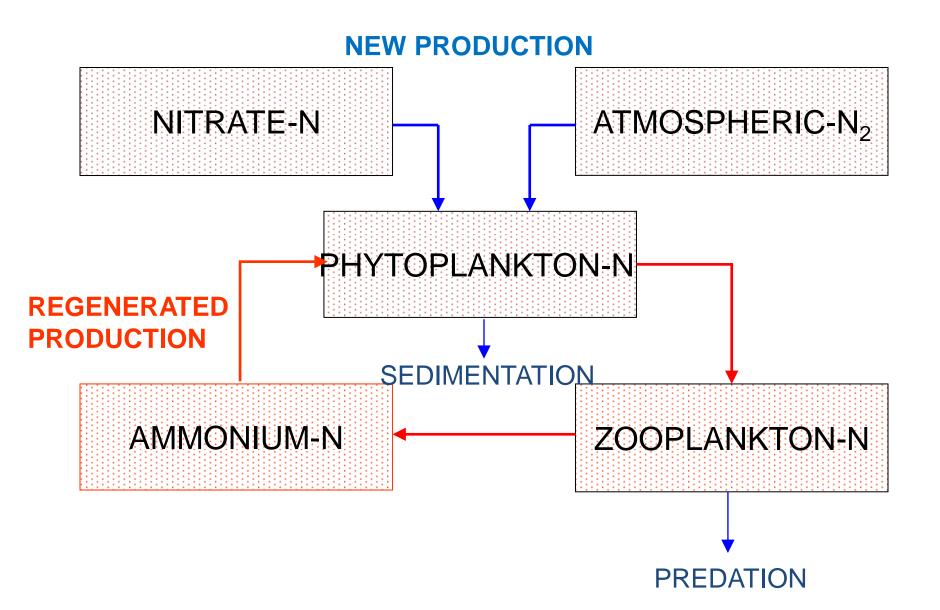
#### **Outline**

- 1. Background: nitrogen cycle in the ocean
- 2. Background data from San Francisco Bay
- 3. Physiological and experimental basis for effect of ammonium on nitrate uptake by phytoplankton
- 4. River Transects
- 5. Suisun Bay spring bloom studies
- 6. Suisun Bay conceptual model
- 7. Suisun Bay NH<sub>4</sub>/NO<sub>3</sub> model
- 8. Nutrient stoichiometric ecosystem model
- 9. SMORE salmon model
- 10. COSiNE model

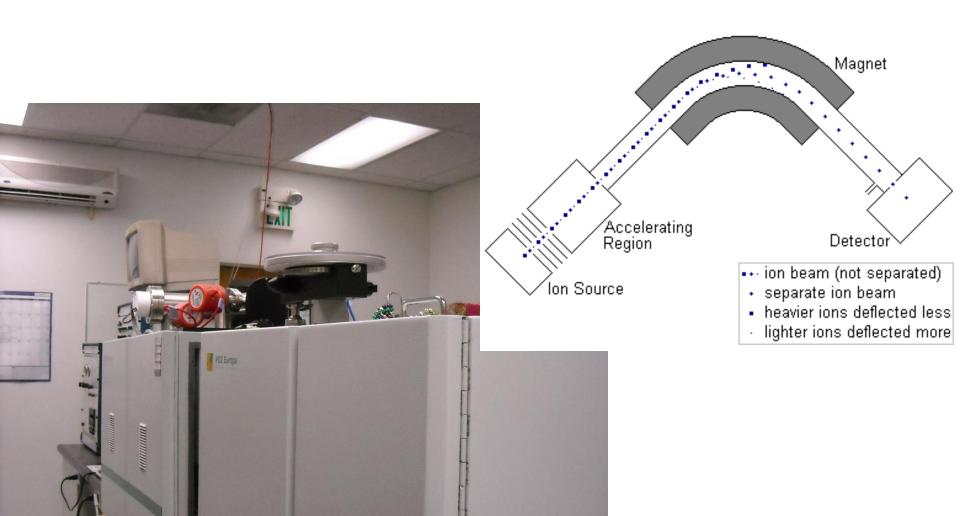
#### Aquatic Nitrogen Cycle



#### New and Regenerated Production



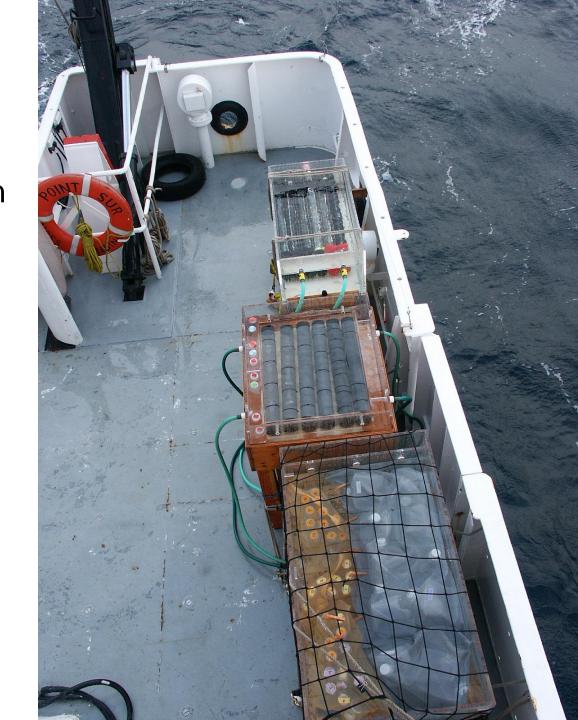
# Use of tracers: can track new and regenerated production with N15 labeled nitrate and ammonium measured with mass spectrometry





sample water

Incubate water sample containing phytoplankton with 15N labeled nitrate or ammonium, or 13C bicarbonate (C fixation)





#### Filter out the phytoplankton

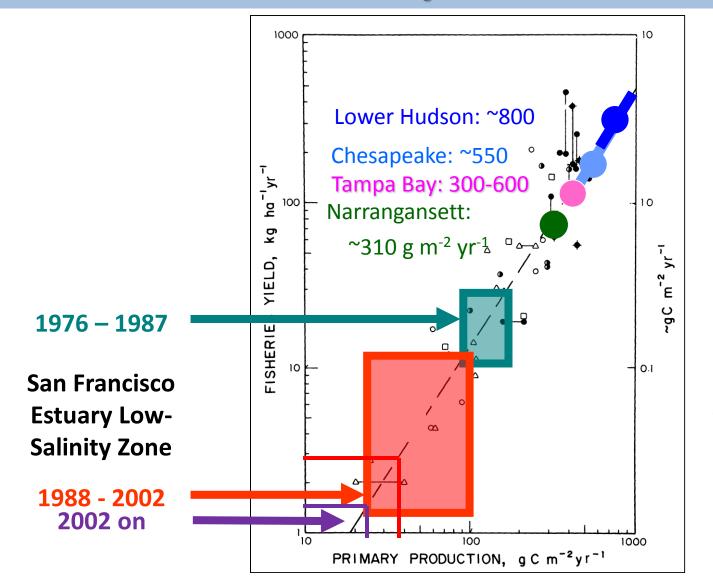


#### San Francisco Estuary

The conventional wisdom for nutrients and primary productivity by phytoplankton in the San Francisco estuary is that:

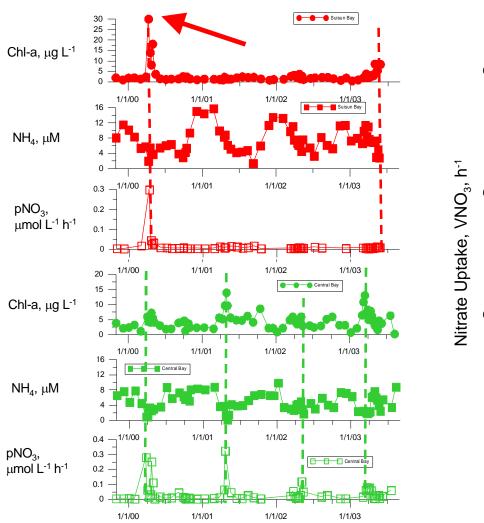
- Nutrients don't matter as light is limiting, and nutrients are always in excess
- The composition of the DIN pool is unimportant since nitrate and ammonium can be used equallyworldwide
- Corbula amurensis (Asian clam) invasion was responsible for the collapse of the primary productivity in Suisun Bay in 1987

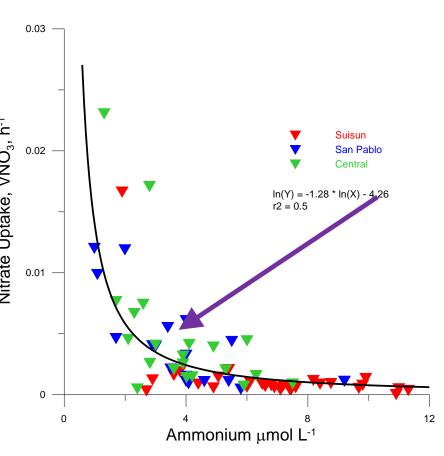
#### Fishery yield directly related to primary production Primary production is the foundation of a healthy estuary



Adapted from Nixon 1988 by Cloern, Parker and others

## We observed in Suisun in 2000, that spring blooms happen when NH₄ is low

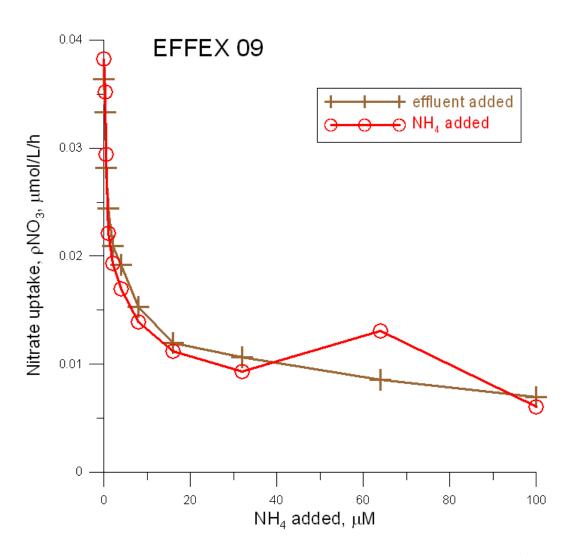




Chl accumulation (dotted line) with low NH<sub>4</sub> Phytoplankton need to access NO<sub>3</sub>.

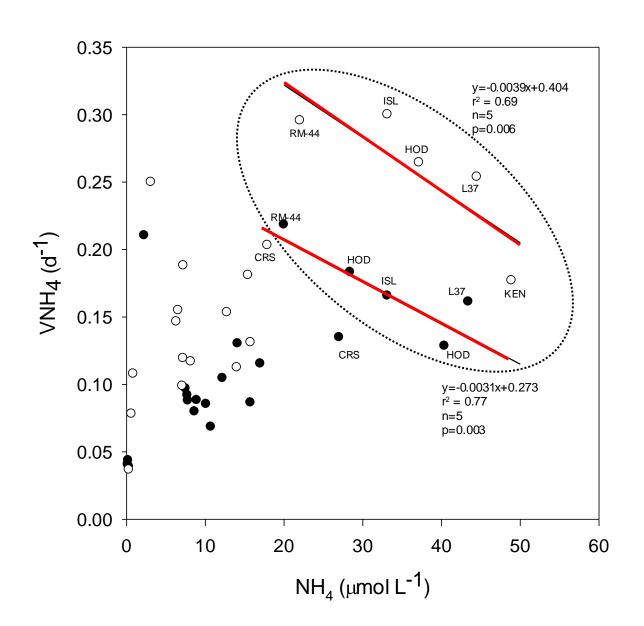
Nitrate uptake increases, once NH<sub>4</sub> is below an inhibitory concentration

### The same relationship occurs with dilutions of effluent or NH₄Cl

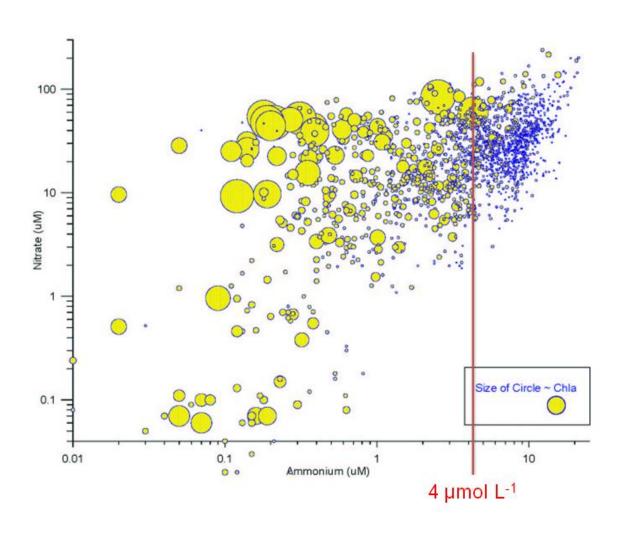


nitrate uptake decreases with high NH<sub>4</sub> whether NH<sub>4</sub> is in effluent or alone

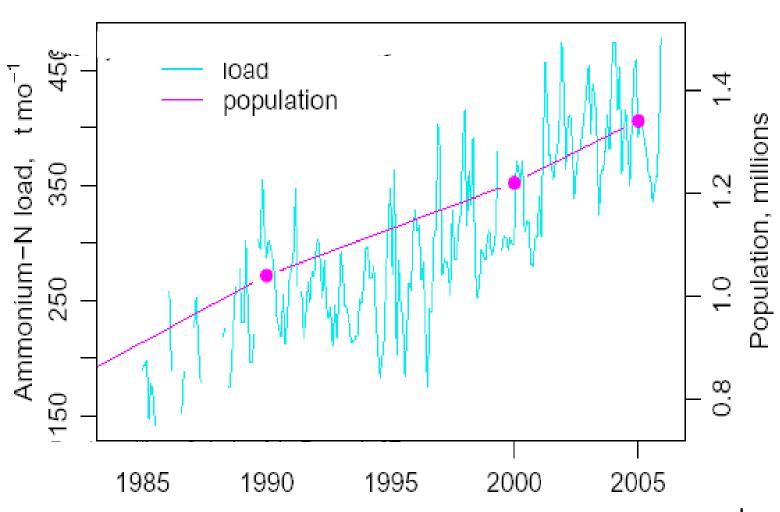
#### High NH₄ can result in decreased NH₄ uptake



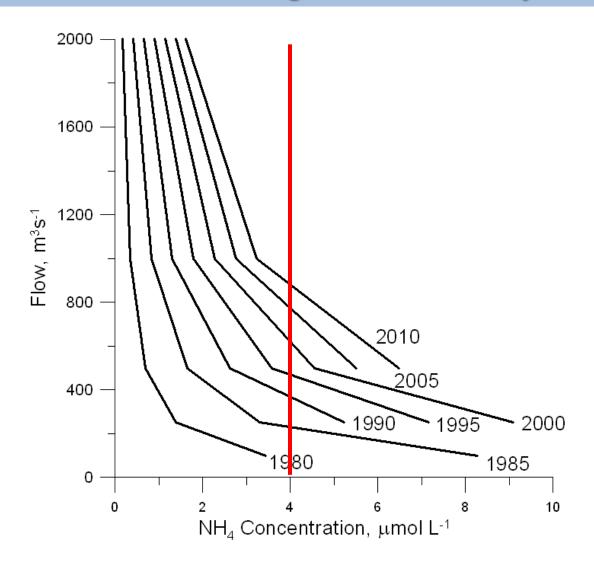
#### Cloern Data for SFE – more chlorophyll (bigger circles) with less ammonium (NH<sub>4</sub>)



### Ammonium loading has increased into Sacramento River along with population



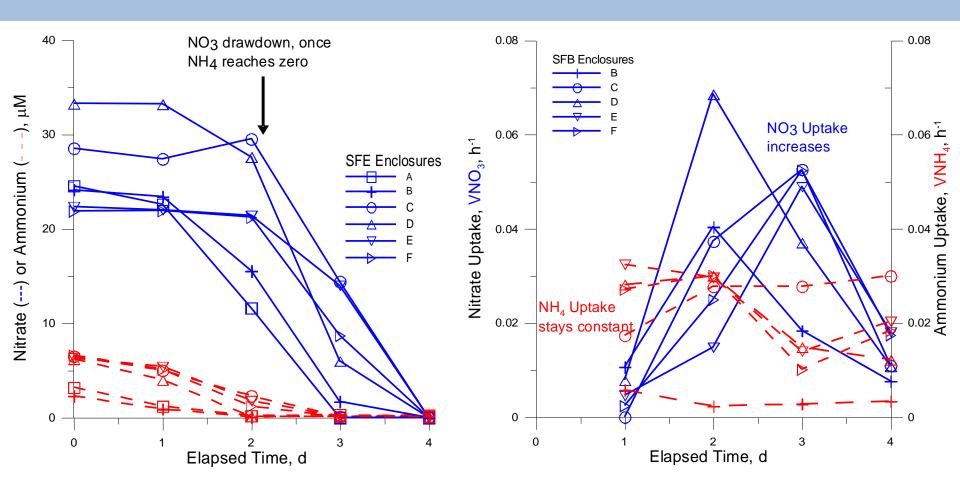
#### NH<sub>4</sub> concentrations at Suisun Bay calculated from SRWWTP discharge in different years



As the discharge increases, the flow needed for 4 µmol L<sup>-1</sup> (ie blooms) increases)

#### In Suisun Bay, chlorophyll decreasing D4 (Sac @ Pt. Sac) Mar-May Dec-Feb Jun-Aug Sep-Nov 25 20 Chl a (ug/L) 15 food limitation for zooplankton 5 1975-W 1982-W 1984-W 1985-D 1986-W 1987-D 1991-D 2000-W 2001-D 2002-D 1978-W 1981-D 1988-D **Q-686** 1990-D 1993-W 1995-W 1996-W 1997-W 1998-W 1999-W 1983-W 1992-D 1994-D 1979-D/W 1980-W 2003-W/D Year

#### Central Bay Enclosure Experiments

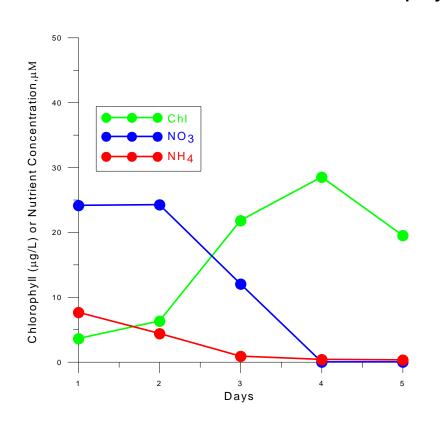


Nitrate drawdown starts once NH<sub>4</sub> is reduced below inhibitory values

Nitrate uptake exceeds ammonium uptake

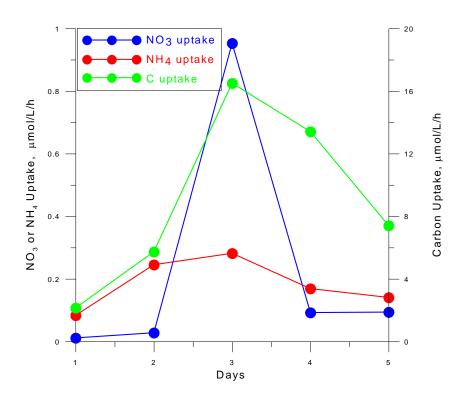
### Chlorophyll accumulation and phytoplankton productivity in Central Bay enclosures

#### Nutrient drawdown and chlorophyll



 $NH_4$  decreases, then when  $NH_4 \sim 4 \mu m$ ,  $NO_3$  drawdown starts on Day 2 and chlorophyll biomass increases

#### Nutrient uptake and C fixation

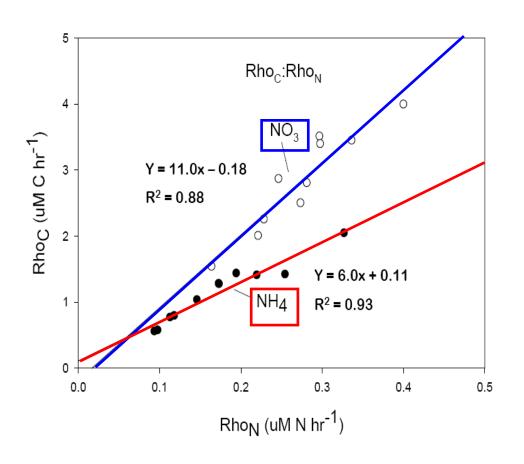


NO<sub>3</sub> uptake is greater than NH<sub>4</sub> uptake. C uptake tracks NO<sub>3</sub> uptake.

June 2007

### Carbon fixation is greater when growth is on NO<sub>3</sub> vs NH<sub>4</sub>





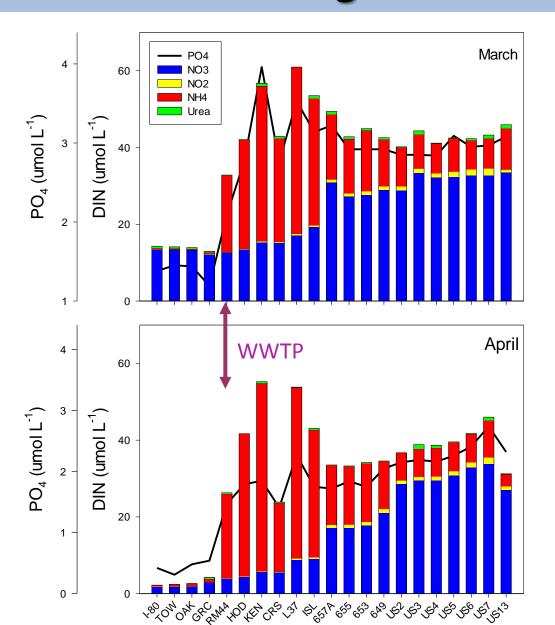
Carbon fixation (rho C) vs NO<sub>3</sub> or NH<sub>4</sub> (rho N) uptake in enclosures in the Delaware Estuary (from Parker, 2004)

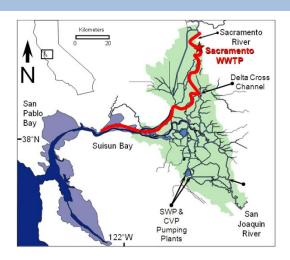
#### Required sequence for bloom formation in SFE

- 1) Phytoplankton biomass buildup by uptake of NH<sub>4</sub> (e.g. from improving irradiance, better water column stability)
- 2) NH<sub>4</sub> concentrations decline to below 4 μmol L<sup>-1</sup>
- 3) Nitrate (NO<sub>3</sub>) and NH<sub>4</sub> uptake produce rapid bloom of chlorophyll

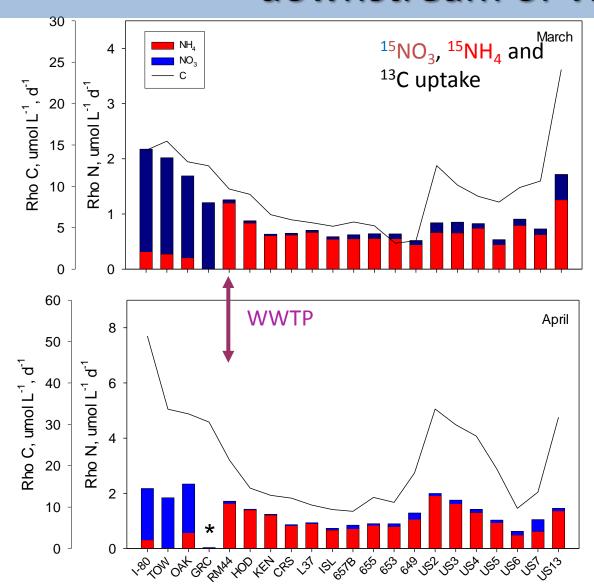


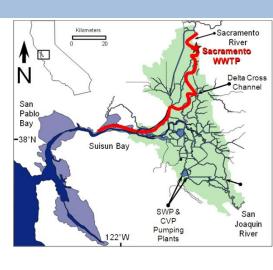
### Change in contribution of NO<sub>3</sub> and NH<sub>4</sub> to total DIN as go downstream



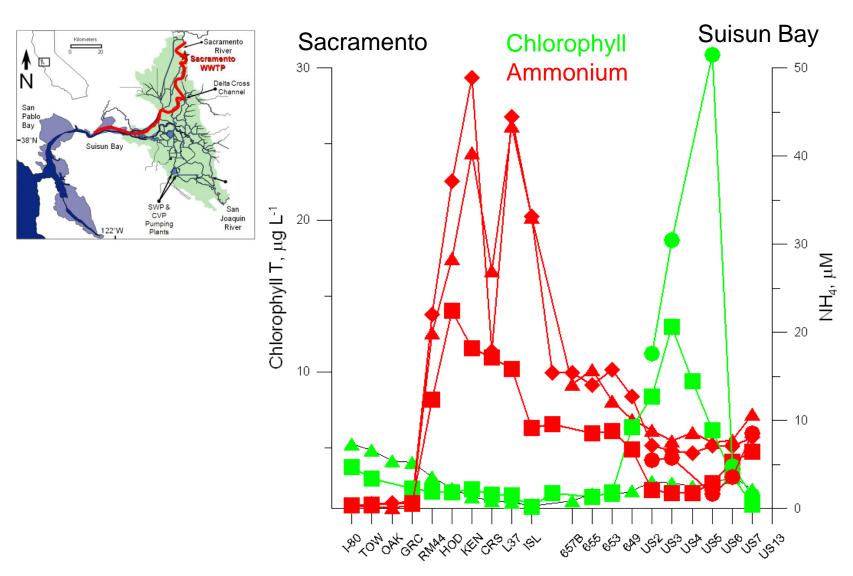


## Shift from uptake of NO<sub>3</sub> to NH<sub>4</sub> uptake system with low primary productivity (C uptake) downstream of WWTP



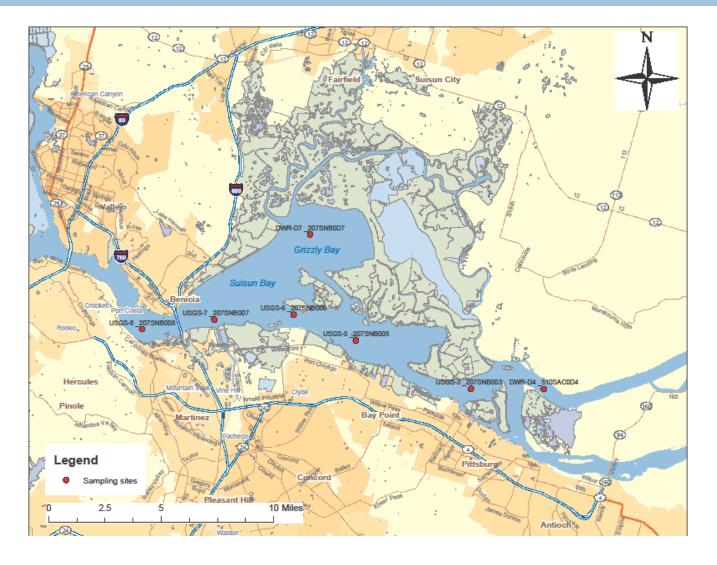


#### Patterns downstream

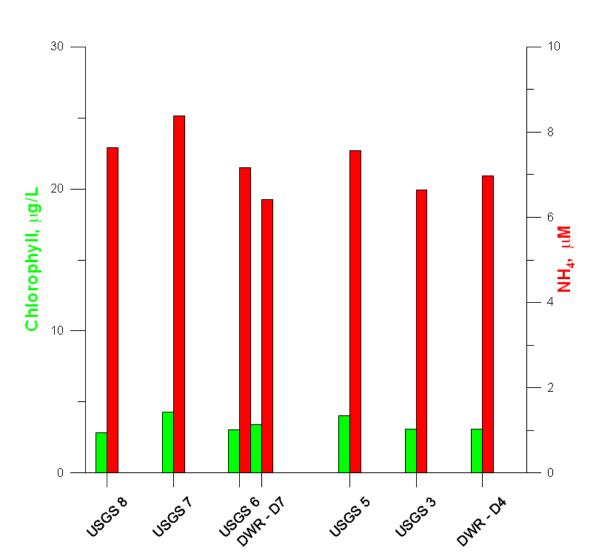


Spring transects sampled in 2009 and 2010

## Suisun Bay spring bloom studies 2010 and 2011

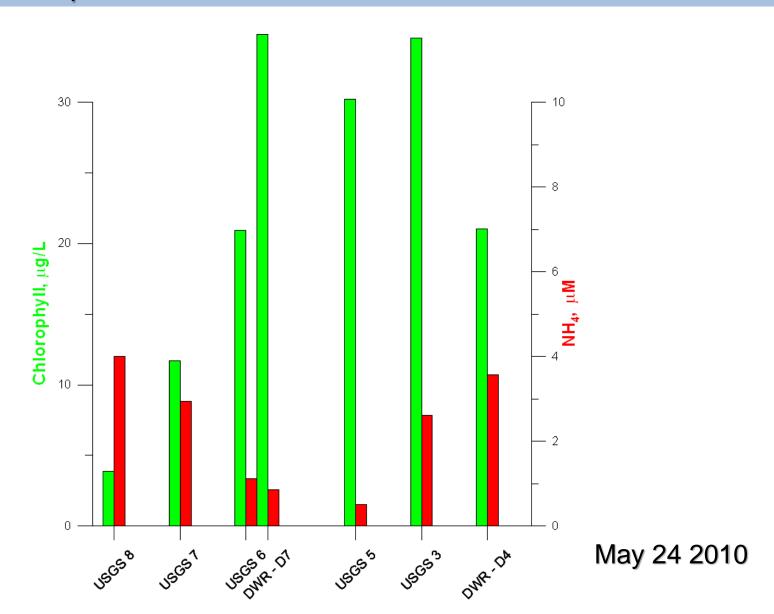


### With high NH<sub>4</sub> concentrations, there was low chlorophyll

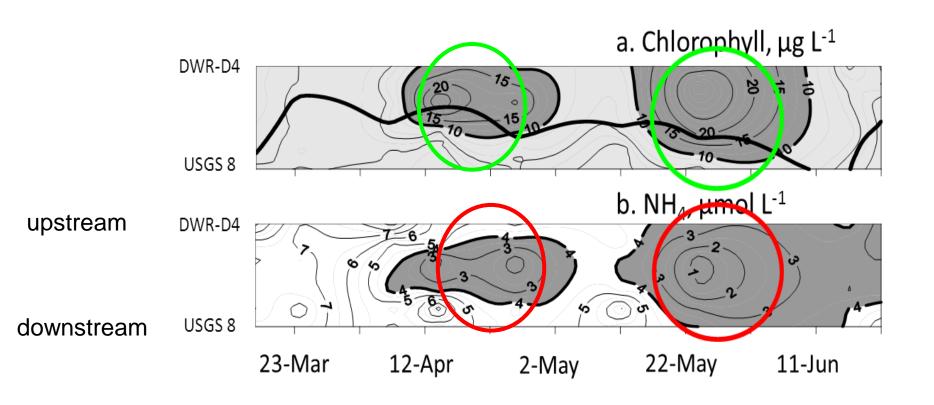


March 24 2010

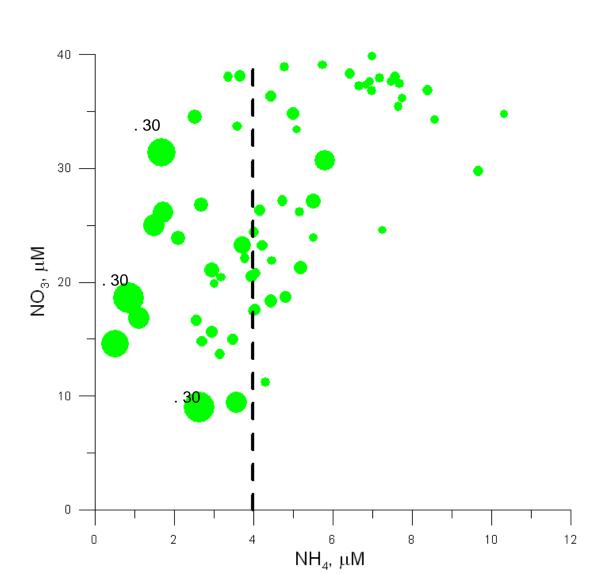
### Phytoplankton Blooms in 2010 occurred with low NH<sub>4</sub> concentrations - as in 2000



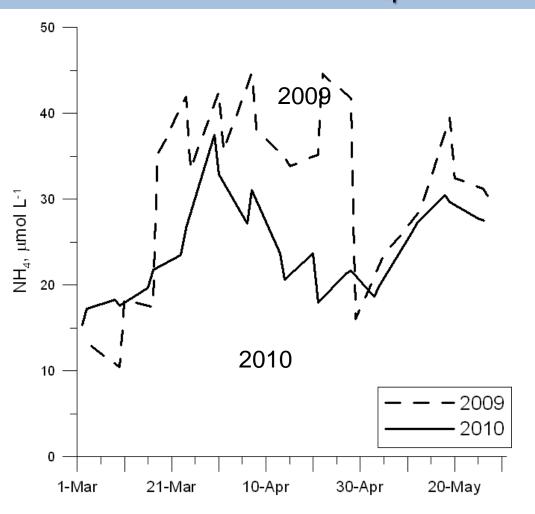
#### In Suisun Bay, blooms where NH<sub>4</sub> < 4 µmol L<sup>-1</sup> in 2010



## At the height of the bloom NH<sub>4</sub> was < 4 μmol L<sup>-1</sup> with high chlorophyll concentrations (~ 30 μg L<sup>-1</sup>); about 20 μmol L<sup>-1</sup> NO<sub>3</sub> was drawndown



## We calculated that in 2010 there was a decline in NH₄ in Sac R near the SR WTP due to increased flow and a decline in NH₄ discharge



SR WTP later explained that they had reduced NH<sub>4</sub> discharge by 12% due to changes in treatment practices!

# Criteria for phytoplankton to bloom in Suisun Bay (i.e. chlorophyll > 10 µg L<sup>-1</sup>), assuming adequate light

- 1) Loading of ammonium must not exceed capacity of the phytoplankton population to take it up (or NH<sub>4</sub> concentration will increase)
- 2) The inflowing concentration of ammonium must be close to 4 µmol L<sup>-1</sup>
- 3) Flow must be less than the washout rate; i.e. basin dilution no greater than phytoplankton growth rate

#### Simplified basin model for NH₄ criteria for blooms

NH<sub>4</sub> input from rivers

- 1) NH<sub>4</sub> per day, tons N d<sup>-1</sup>
- 2) Concentration µmol L<sup>-1</sup>



Flow, m<sup>3</sup>d<sup>-1</sup>

Surface area 1.7x10<sup>8</sup> m<sup>2</sup> Volume 9.9x10<sup>8</sup>m<sup>3</sup>

Loading NH₄ input from rivers / surface area

Phytoplankton uptake=VNH<sub>4</sub> \* biomass as N or chl

NH<sub>4</sub> outflow= NH<sub>4</sub> input from rivers minus phytoplankton uptake



### Comparing NH<sub>4</sub> loading with phytoplankton capacity to take up NH<sub>4</sub>

Range of loadings to Suisun Bay (from SacRegional WTP, corrected for nitrification)

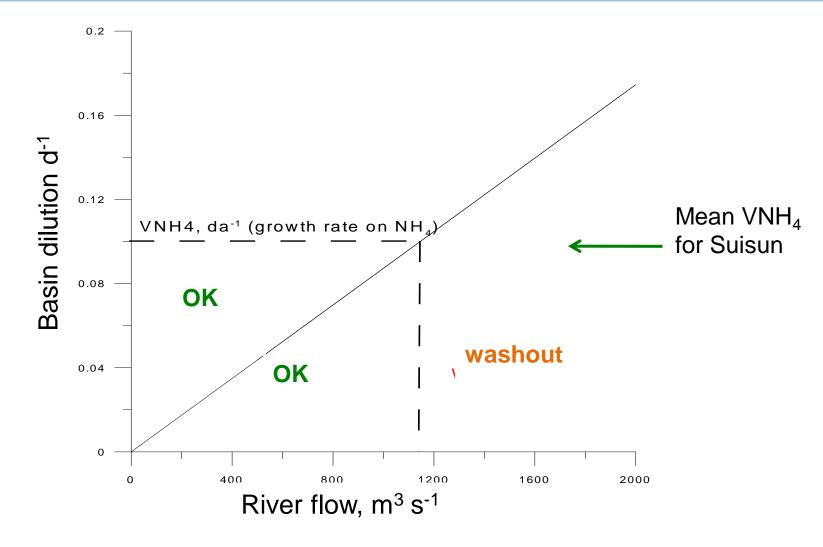
tons N day⁻¹	mmolm <sup>-2</sup> d <sup>-1</sup>
5 (ca 1980)	0.53
10	1.05
15 (present)	1.58

Range of phytoplankton uptake in Suisun Bay (from Wilkerson et al. 2007)

*mmolm*<sup>-2</sup>*d*<sup>-1</sup> 0.49-1.2

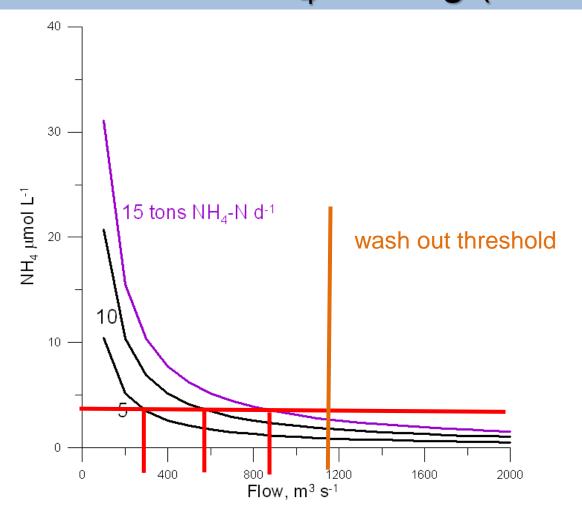
Loading must be less than phytoplankton uptake capacity (or NH<sub>4</sub> concentration will increase)

### Comparing basin dilution with phytoplankton growth rate on NH<sub>4</sub>



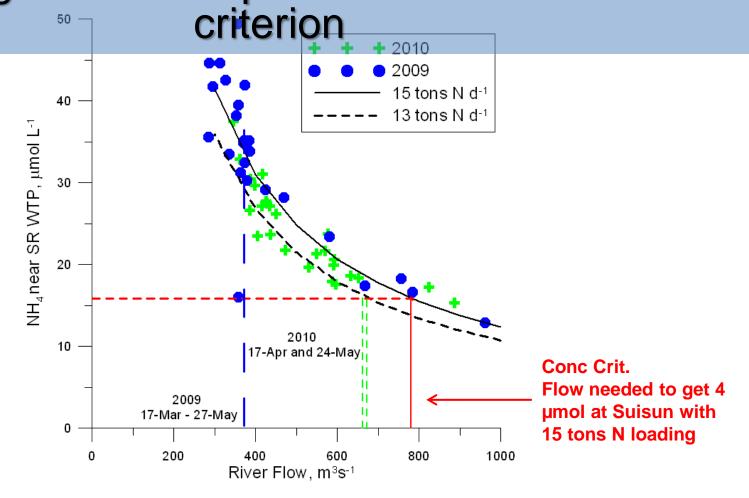
Basin dilution no greater than phytoplankton growth rate (or will washout)

### Threshold flows required for 4 µmol L<sup>-1</sup> NH<sub>4</sub> at Suisun with different NH<sub>4</sub> loading (5-15 tons d<sup>-1</sup>)



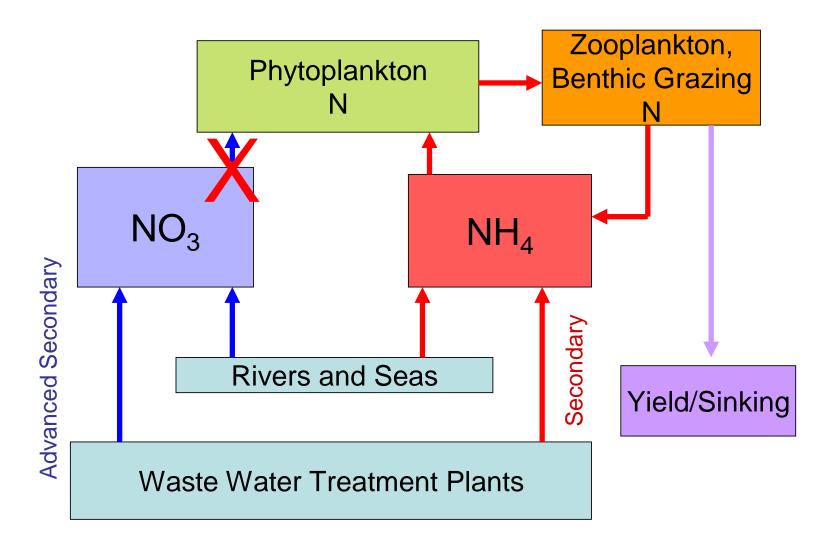
With increasing loads the flow window gets smaller.
With 15 tons N loading, flows need to be between ~825 and ~1100 m<sup>3</sup> s<sup>-1</sup>

# NH<sub>4</sub> in the river at the WTP vs. river flow with curves showing relationship for different N loadings with the 4 µmol L<sup>-1</sup> concentration



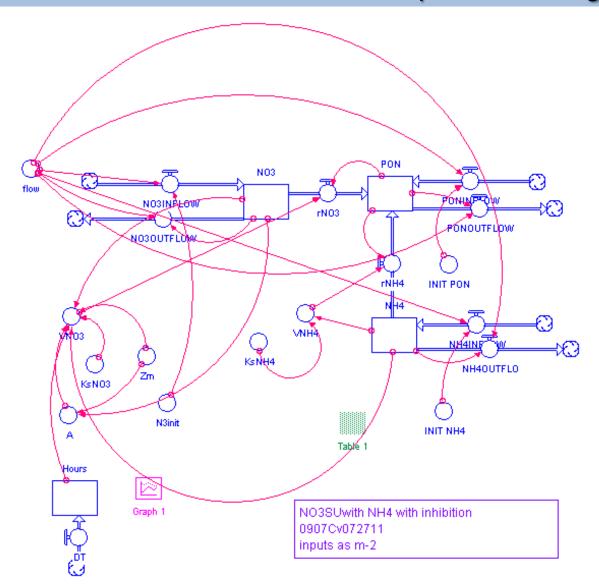
Flow during 2010 blooms was sufficient to meet the concentration criterion of 4  $\mu$ mol at Suisun with ~13 tons N loading. Flow too low in 2009

### Simplified Estuarine N Cycle



Cutting off phytoplankton access to NO<sub>3</sub> reduces potential phytoplankton biomass by 80%

# Suisun Bay NH<sub>4</sub>/NO<sub>3</sub> model to describe NH<sub>4</sub> and NO<sub>3</sub> interactions



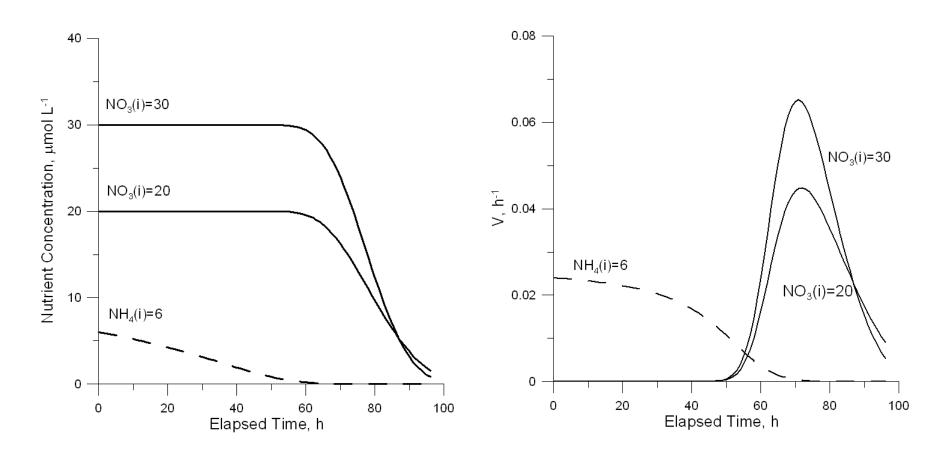
#### **Basic Equations**

NH4 uptake, Michaelis Menten VNH<sub>4</sub>=V<sub>maxNH4</sub>\*NH<sub>4</sub>/(NH<sub>4</sub>+K<sub>S</sub>)

NO<sub>3</sub> uptake, 1)Acceleration kinetics  $VNO_3 = NO_3(i) + A*t$   $A = 4 \times 10^{-5*}NO_3 + 4 \times 10^{-5}$ 2) Inhibition by  $NH_4$ ,  $VNO_3*exp^{-5.59*NH4}$  Model can be run in 3 modes:

- 1) Flow set to 0, simulates enclosure experiments
- 2) Flow set to proportion of volume, simulates a fully mixed bay
- 3) Flow set to proportion of volume, inputs are as surface area integrated values, Simulates fully mixed bay with phytoplankton productivity restricted by irradiance

#### 1) Flow set to 0, simulates enclosure experiments

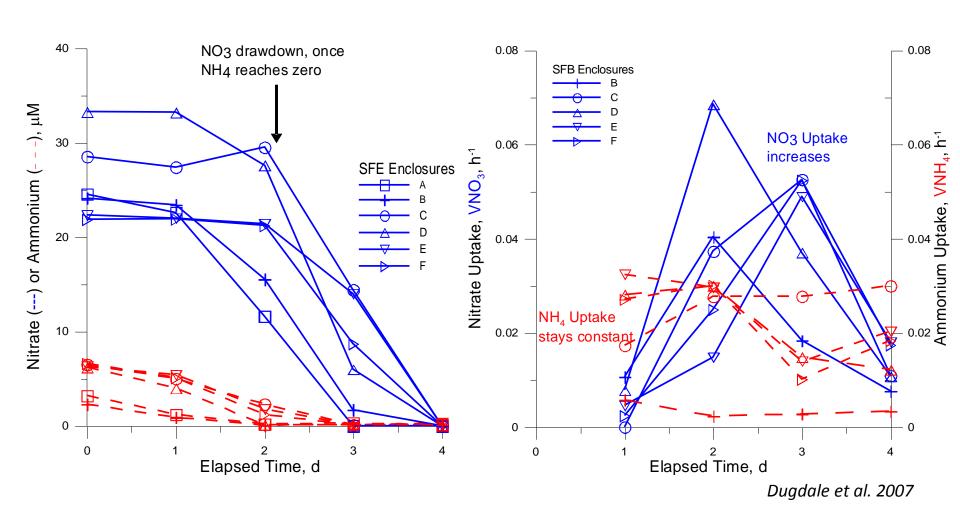


Nitrate drawdown starts once NH<sub>4</sub> is reduced below inhibitory values

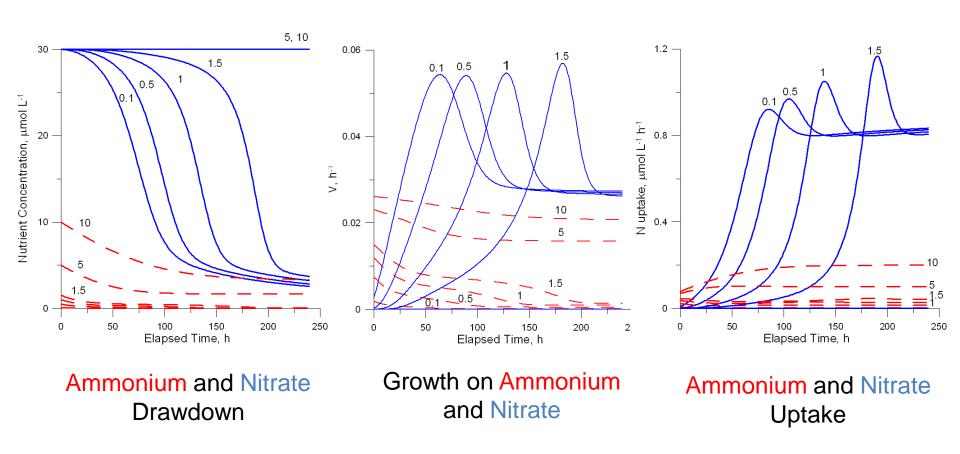
Nitrate uptake exceeds ammonium uptake

#### **Central Bay Enclosures**



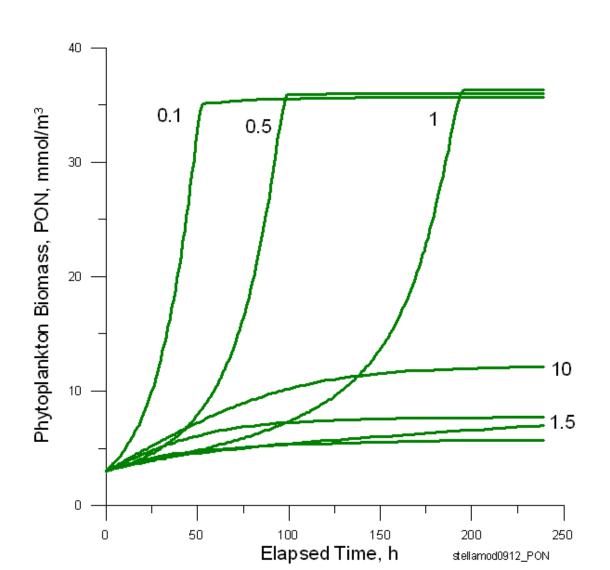


## 2) Flow set to proportion of volume, simulates a fully mixed bay

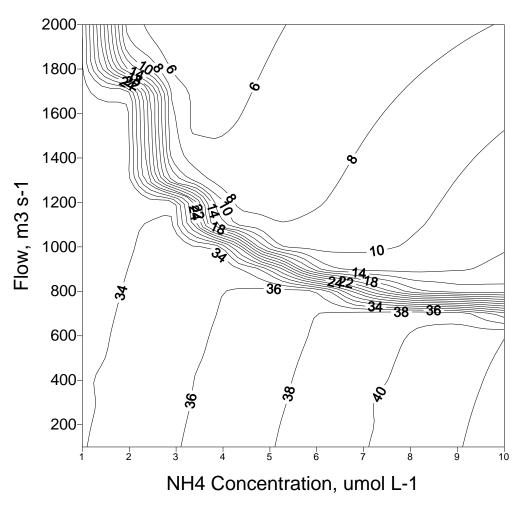


Numbers are increasing inflowing ammonium concentrations

## 2) Flow set to proportion of volume, simulates a fully mixed bay: two states of biomass accumulation

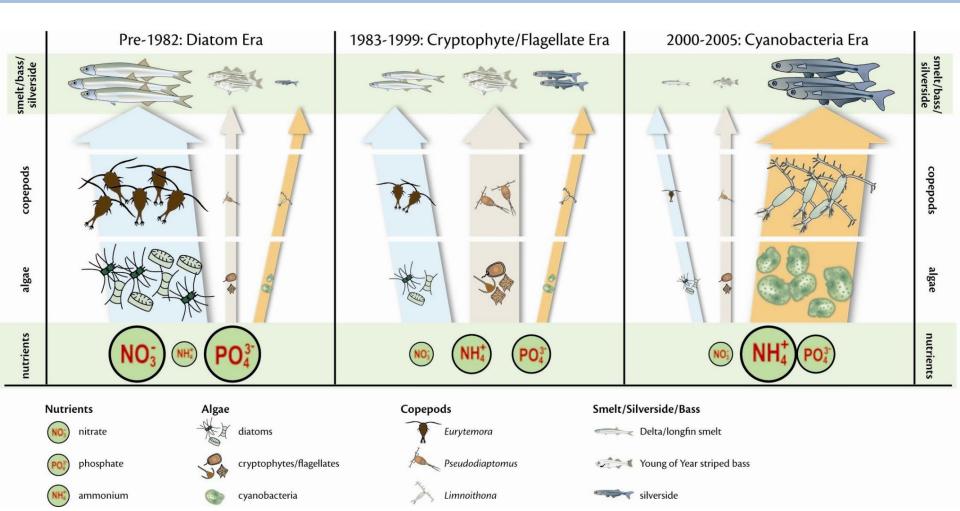


# 3) Flow set to proportion of volume, inputs are as surface area integrated values, simulates fully mixed bay with phytoplankton productivity restricted by irradiance

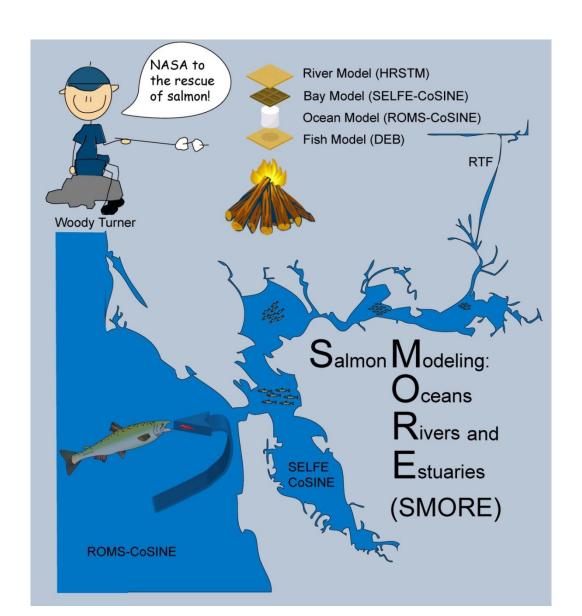


Sharp boundaries in biomass (the contours) at critical flow and NH<sub>4</sub> interactions

# Nutrient stoichiometric model With increasing NH<sub>4</sub> and decrease in PO<sub>4</sub>, the phytoplankton and food webs have changed

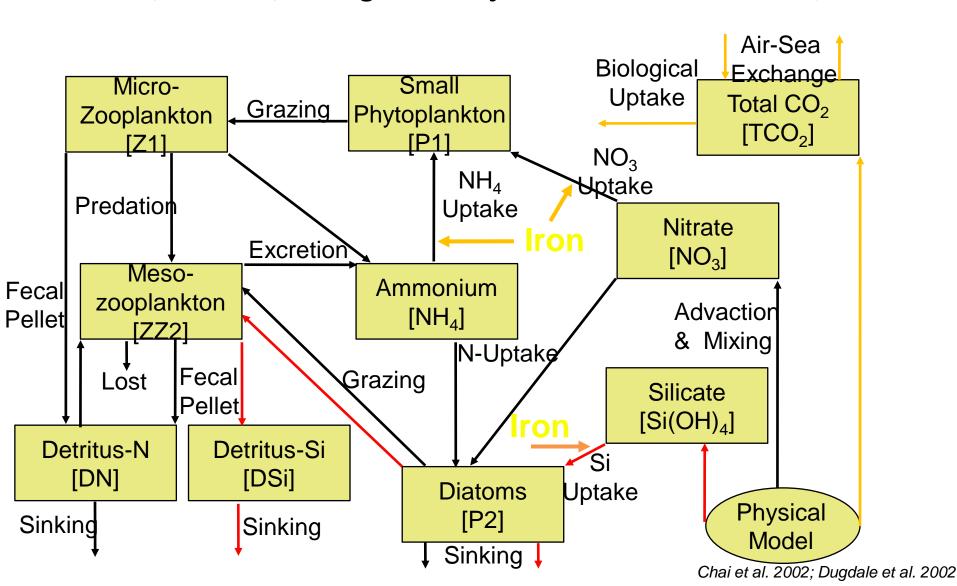


## SMORE salmon model: new project to combine a lot of models to simulate salmon success from egg to adult

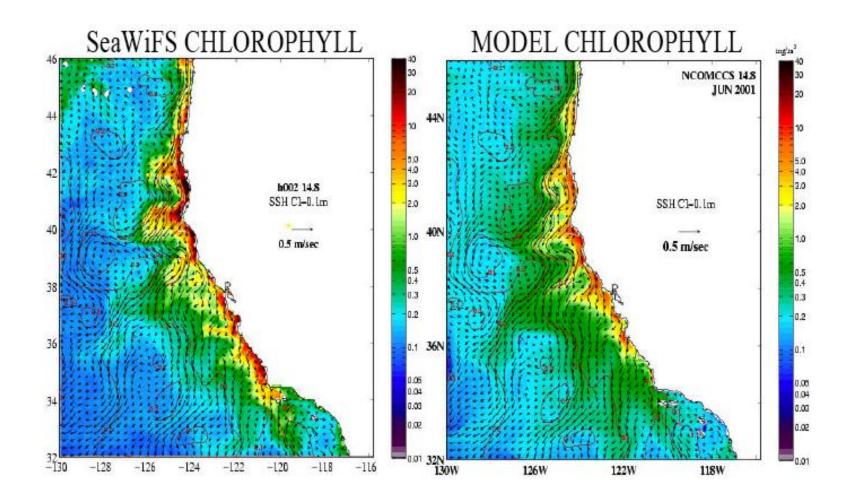


### The lower trophic model to be used will be CoSiNE which will need to be modified for the estuary and rivers

Carbon, Silicate, Nitrogen Ecosystem Model CoSiNE,



#### Example of CoSiNE/NCOMCCS in Coastal Ocean



#### Acknowledgements

- Calfed/Delta Science Program
- InterEcological Agency
- State and Federal Water Contractors
- San Francisco Bay Regional Water Quality Board
- Central Valley Regional Water Quality Board